OPTIMUM TIMING FOR CO₂-EOR AFTER WATERFLOODING
AND SOAKING EFFECT ON MISCIBLE CO₂ FLOODING
IN A TIGHT SANDSTONE FORMATION

A Thesis
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In Partial Fulfillment of the Requirements for the
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by
Zeya Li
Regina, Saskatchewan
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Zeya Li, candidate for the degree of Master of Applied Science in Petroleum Systems Engineering, has presented a thesis titled, *Optimum Timing for CO₂-EOR After Waterflooding and Soaking Effect on Miscible CO₂ Flooding in a Tight Sandstone Formation*, in an oral examination held on April 14, 2014. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner: Dr. Amornvadee Veawab, Environmental Systems Engineering

Supervisor: Dr. Yongan Gu, Petroleum Systems Engineering

Committee Member: Dr. Gang Zhao, Petroleum Systems Engineering

Committee Member: Dr. Hussameldin Ibrahim, Industrial Systems Engineering

Chair of Defense: Dr. Hairuo Qing, Department of Geology
ABSTRACT

In continuous CO$_2$ secondary flooding, severe viscous fingering and early CO$_2$ breakthrough (BT) occur due to an unfavourable mobility contrast between the injected CO$_2$ and the crude oil. The oil recovery is limited after CO$_2$ BT, which is attributed to the gas channeling problem. In continuous CO$_2$ tertiary flooding, the previously injected water helps to control the mobility of the subsequently injected CO$_2$. On the other hand, it hinders the mutual interactions between the residual oil and the subsequently injected CO$_2$ and thus affects the tertiary oil recovery.

This thesis experimentally studied the mutual interactions between the light oil/reservoir brine and CO$_2$ and the technical optimization of CO$_2$ enhanced oil recovery (CO$_2$-EOR) process, which included the optimum timing for CO$_2$-EOR after waterflooding and soaking effect on miscible CO$_2$ flooding in a tight sandstone formation. First, the saturation pressure ($P_{sat}$), oil-swelling factor (SF), gas–oil ratio (GOR) of CO$_2$-saturated light oil, and gas–water ratio (GWR) of CO$_2$-saturated reservoir brine were measured by using a PVT system. Second, the viscosities of CO$_2$-saturated light oil with different CO$_2$ concentrations were measured by using a capillary viscometer. Third, the equilibrium interfacial tensions (IFTs) between the light oil/reservoir brine and CO$_2$ were measured at different equilibrium pressures and the actual reservoir temperature by applying the axisymmetric drop shape analysis (ADSA) technique for the pendant oil drop case. Finally, five coreflood tests were performed to determine the optimum timing for miscible CO$_2$-EOR after waterflooding and six coreflood tests were conducted to examine CO$_2$-soaking effect on miscible CO$_2$ flooding in a tight sandstone formation, respectively.
The experimental results showed that $P_{\text{sat}}$ and oil SF of CO$_2$-saturated light oil were increased respectively in the ranges of 4.97–8.44 MPa and 1.14–1.34 when CO$_2$ concentration in the light oil–CO$_2$ system was increased in the range of 38.94–60.46 mol.%. The measured GOR of CO$_2$-saturated light oil was found to be approximately six times of the measured GWR of CO$_2$-saturated reservoir brine at the same pressure and temperature. The respective viscosities of CO$_2$-saturated light oils with 38.94 and 60.46 mol.% CO$_2$ concentrations were reduced to lower than 16% and 10% of the original dead light oil viscosity at the same reservoir temperature. The measured equilibrium IFT between the light oil and CO$_2$ was about one third to one tenth of that between the reservoir brine and CO$_2$ under the same test conditions. By comparing the total oil recovery factor (RF) of waterflooding and CO$_2$ flooding in terms of the original-oil-in-place (OOIP), the oil RF of CO$_2$ flooding in terms of the residual-oil-in-place (ROIP), and the pore volume (PV) of CO$_2$ BT from the beginning of CO$_2$ flooding, it is found that the optimum timing for starting miscible CO$_2$ tertiary flooding is when waterflooding reaches half of its maximum secondary oil RF. It was found that in the coreflood tests without CO$_2$ soaking, a large amount of oil was produced in the first PV of CO$_2$ injection, whereas only a low oil RF of 0.77–6.10% was obtained in the second PV of CO$_2$ injection. In the coreflood tests with CO$_2$ soaking, the composite sandstone reservoir core plugs with the residual light oil, reservoir brine, and remaining CO$_2$ were soaked for 24 h after the first PV of CO$_2$ injection. A high oil RF of 11.05–14.74% was achieved in the second PV of CO$_2$ injection. Among the six CO$_2$ coreflood tests, pre-waterflooding plus CO$_2$ tertiary flooding with CO$_2$ soaking resulted in the highest oil RF, which was attributed to the mobility-control effect of pre-waterflooding and CO$_2$-soaking effect.
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DEDICATION

To my parents, for their constant love and support.
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NOMENCLATURE

Notations

\( k \) Permeability, mD

\( L \) Length of the capillary viscometer, m

\( m_{\text{brine}} \) Mass of brine, g

\( m_{\text{CO}_2} \) Mass of \( \text{CO}_2 \), g

\( m_{\text{CO}_2}^f \) Final mass of \( \text{CO}_2 \) in the PVT cell, g

\( m_{\text{CO}_2}^i \) Initial mass of \( \text{CO}_2 \) in the PVT cell, g

\( m_{\text{mix}} \) Mass of the mixture of light oil and \( \text{CO}_2 \), g

\( m_{\text{oil}} \) Mass of oil, g

\( M_{\text{W oil}} \) Molecular weight of the light crude oil, g/mol

\( N_{\text{ca}} \) Capillary number

\( P_{\text{cell}} \) Pressure of PVT cell, MPa

\( P_{\text{eq}} \) Equilibrium pressure, MPa

\( P_{\text{ini}} \) Initial pressure, MPa

\( P_{\text{max}} \) First-contact miscibility pressure, MPa

\( P_{\text{prod}} \) Production pressure, MPa

\( P_{\text{sat}} \) Saturation pressure, MPa

\( P_{\text{sc}} \) Pressure at the standard conditions, kPa

\( q_{\text{CO}_2} \) \( \text{CO}_2 \) injection rate, cm\(^3\)/min

\( q_g \) Average produced gas flow rate, cm\(^3\)/min

\( q_{\text{mix}} \) Volume flow rate of \( \text{CO}_2 \)-saturated light oil, cm\(^3\)/min

\( q_{\text{oil}} \) Oil injection rate, cm\(^3\)/min

\( q_w \) Water volume flow rate, cm\(^3\)/min
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{water}}$</td>
<td>Water injection rate, cm$^3$/min</td>
</tr>
<tr>
<td>$Q_w$</td>
<td>Cumulative water production, cm$^3$</td>
</tr>
<tr>
<td>$r_{\text{eff}}$</td>
<td>Effective radius of the capillary viscometer, m</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Correlation coefficient</td>
</tr>
<tr>
<td>$S_{\text{oi}}$</td>
<td>Initial oil saturation, %</td>
</tr>
<tr>
<td>$S_{\text{wc}}$</td>
<td>Connate water saturation, %</td>
</tr>
<tr>
<td>$t_{\text{soaking}}$</td>
<td>Soaking time, h</td>
</tr>
<tr>
<td>$T_{\text{lab}}$</td>
<td>Laboratory temperature, °C</td>
</tr>
<tr>
<td>$T_{\text{res}}$</td>
<td>Reservoir temperature, °C</td>
</tr>
<tr>
<td>$T_{\text{sc}}$</td>
<td>Temperature at the standard conditions, 15.6 °C</td>
</tr>
<tr>
<td>$v$</td>
<td>Liner flow velocity, cm/s</td>
</tr>
<tr>
<td>$v_{\text{mix}}$</td>
<td>Mass-based specific volume of the mixture, cm$^3$/g</td>
</tr>
<tr>
<td>$V_{\text{CO}_2}$</td>
<td>Volume of CO$_2$ at the atmospheric pressure and laboratory temperature, cm$^3$</td>
</tr>
<tr>
<td>$V_{\text{mix}}$</td>
<td>Volume of the mixture of light oil and CO$_2$, cm$^3$</td>
</tr>
<tr>
<td>$V_{\text{oil}}$</td>
<td>Volume of the light oil, cm$^3$</td>
</tr>
<tr>
<td>$w_{\text{asp}}$</td>
<td>Asphaltene content, wt.%</td>
</tr>
<tr>
<td>$z_{\text{CO}_2}$</td>
<td>Mole percentage of CO$_2$ in the light oil–CO$_2$ system, mol.%</td>
</tr>
<tr>
<td>$z_{\text{oil}}$</td>
<td>Mole percentage of the light crude oil in the light oil–CO$_2$ system, mol.%</td>
</tr>
</tbody>
</table>

**Greek letters**
\( \gamma_{\text{brine-CO}_2} \)  
Equilibrium interfacial tension between reservoir brine and CO\(_2\), mJ/m\(^2\)

\( \gamma_{\text{eq}} \)  
Equilibrium interfacial tension between light oil and CO\(_2\), mJ/m\(^2\)

\( \gamma_{\text{oil-CO}_2} \)  
Equilibrium Interfacial tension between light oil and CO\(_2\), mJ/m\(^2\)

\( \Delta P \)  
Pressure drop between the inlet and outlet of the capillary viscometer during viscosity measurement, kPa

\( \mu_{\text{mix}} \)  
Viscosity of the mixture of light oil and CO\(_2\), mPa·s

\( \mu_{\text{oil}} \)  
Viscosity of crude oil, mPa·s

\( \mu_{\text{w}} \)  
Viscosity of distilled water, mPa·s

\( \rho_{\text{brine}} \)  
Density of brine, g/cm\(^3\)

\( \rho_{\text{CO}_2} \)  
Density of CO\(_2\) at the standard conditions, g/cm\(^3\)

\( \rho'_{\text{CO}_2} \)  
Density of CO\(_2\) at the atmospheric pressure and laboratory temperature, g/cm\(^3\)

\( \rho_{\text{oil}} \)  
Density of the crude light oil, g/cm\(^3\)

\( \phi \)  
Porosity, %

**Subscripts**

asp  
Asphaltene

brine  
Brine

cell  
PVT cell

eff  
Effective

eq  
Equilibrium
ini  Initial
lab  Laboratory
m    Mass
max  Maximum
mix  Mixture
oi   Initial oil
oil  Oil
prod Production
res  Reservoir
sat  Saturation
sc   The standard condition
w    Water
water Water
wc   Connate water

Superscripts
f    Final condition
i    Initial condition

Acronyms
atm  Atmospheric pressure
ADSA  Axisymmetric drop shape analysis
ASTM  American Society for Testing and Materials
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOPD</td>
<td>Barrels of oil per day</td>
</tr>
<tr>
<td>BT</td>
<td>Breakthrough</td>
</tr>
<tr>
<td>CMG</td>
<td>Computer Modelling Group</td>
</tr>
<tr>
<td>CSI</td>
<td>Cyclic solvent injection</td>
</tr>
<tr>
<td>CSP</td>
<td>Cyclic solvent process</td>
</tr>
<tr>
<td>CWI</td>
<td>Carbonated water injection</td>
</tr>
<tr>
<td>DPDVA</td>
<td>Dynamic pendant drop volume analysis</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced oil recovery</td>
</tr>
<tr>
<td>EOS</td>
<td>Equation of state</td>
</tr>
<tr>
<td>FCM</td>
<td>First-contact miscibility</td>
</tr>
<tr>
<td>GOR</td>
<td>Gas–oil ratio</td>
</tr>
<tr>
<td>GWR</td>
<td>Gas–water ratio</td>
</tr>
<tr>
<td>HCs</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>IFT</td>
<td>Interfacial tension</td>
</tr>
<tr>
<td>MCM</td>
<td>Multi-contact miscibility</td>
</tr>
<tr>
<td>MMP</td>
<td>Minimum miscibility pressure</td>
</tr>
<tr>
<td>NSERC</td>
<td>Natural Science and Engineering Research Council</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>OOIP</td>
<td>Original-oil-in-place</td>
</tr>
<tr>
<td>P–R</td>
<td>Peng–Robinson</td>
</tr>
<tr>
<td>RF</td>
<td>Recovery factor</td>
</tr>
<tr>
<td>PDM</td>
<td>Pressure decay method</td>
</tr>
<tr>
<td>PTRC</td>
<td>Petroleum Technology Research Centre</td>
</tr>
<tr>
<td>PV</td>
<td>Pore volume</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>PVT</td>
<td>Pressure–volume–temperature</td>
</tr>
<tr>
<td>R&amp;D</td>
<td>Research and development</td>
</tr>
<tr>
<td>RBA</td>
<td>Rising bubble apparatus</td>
</tr>
<tr>
<td>ROIP</td>
<td>Residual-oil-in-place</td>
</tr>
<tr>
<td>SAG</td>
<td>Soaking-alternating-gas</td>
</tr>
<tr>
<td>SF</td>
<td>Swelling factor</td>
</tr>
<tr>
<td>SWAG</td>
<td>Simultaneous water-alternating-gas</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>TIFF</td>
<td>Tagged image file format</td>
</tr>
<tr>
<td>TLF</td>
<td>Thin liquid films</td>
</tr>
<tr>
<td>VIT</td>
<td>Vanishing interfacial tension</td>
</tr>
<tr>
<td>WAG</td>
<td>Water-alternating-gas</td>
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</table>
CHAPTER 1 INTRODUCTION

1.1 CO₂-Based Oil Recovery

Since the 1950s, CO₂ flooding has been proven to be an effective enhanced oil recovery (EOR) method under some favourable reservoir conditions [Whorton et al., 1952]. There were a total of 114 miscible and 9 immiscible ongoing CO₂-EOR projects in the USA [Kuuskraa, 2012]. In Canada, there are two commercial and ongoing miscible CO₂-EOR projects and at least four CO₂-EOR pilot tests in Alberta and Saskatchewan [Koottungal, 2012]. In 2012, miscible CO₂-EOR processes produced 308,564 barrels of oil per day (BOPD), which accounted for 41% of the total daily oil production of all the EOR methods and surpassed the daily oil production of any other EOR methods in the USA [ABI/INFORM Global, 2012]. In the laboratory studies, miscible CO₂ secondary flooding in the slim-tube tests can reach an oil recovery factor (RF) of 90% [Yellig and Metcalfe, 1980]. The major CO₂-EOR mechanisms include miscible or immiscible displacement, interfacial tension (IFT) reduction, oil viscosity reduction, oil-swelling effect, and light-hydrocarbons (HCs) extraction by supercritical CO₂ [Stalkup, 1983; Green and Willhite, 1998]. It is worthwhile to note that CO₂-EOR projects not only recover the crude oil but also mitigate the greenhouse gas emissions by storing CO₂ underground. It is estimated that CO₂-EOR projects have the potential to recover 1.07 trillion barrels of oil and store 320 billion tonnes of CO₂ in the basins worldwide [Godec et al., 2011].
1.2 Optimum Timing of Miscible CO₂-EOR after Waterflooding

In the oilfield applications, however, CO₂ flooding has several limitations. Technically, both viscous fingering due to an extremely low viscosity of CO₂ and gravity overriding due to a relatively low density of CO₂ under the actual reservoir conditions adversely affect the practical performance of CO₂-EOR [Dellinger et al., 1984]. They result in a poor sweeping efficiency and an early CO₂ breakthrough (BT) in an oil reservoir. Economically, relatively high capital and operating costs for CO₂ acquisition, transportation, storage, and compression also seriously limit the field applications of CO₂-EOR [Holt et al., 2009]. In general, CO₂ flooding is not considered at the beginning of an oilfield development but conducted as a tertiary flooding process after the primary and secondary (i.e., waterflooding) oil recovery processes. Waterflooding is the most economical method to recover the crude oil and maintain the reservoir pressure. The waterflooding process recovers a certain amount of oil, changes the reservoir fluid saturations and thus affects the subsequently applied EOR process. Unlike the connate water, the injected water is continuous and mobile so that it may form water channels after it breaks through the oil reservoir [Tiffin and Yellig, 1983]. The residual oil in the water-swept area is trapped by the injected water and thus becomes immobile [Stalkup, 1970]. At the pore level, the residual oil is surrounded by the injected water, which hinders the mutual interactions between the trapped residual oil and the subsequently injected fluids [Grogan and Pinczewski, 1987]. This phenomenon is referred to as waterblocking effect [Bijeljic et al., 2002]. Hence, the major purpose of CO₂-EOR is to recover the trapped residual oil by overcoming the
waterblocking effect through strong mutual interactions between the reservoir fluids and the injected CO₂.

In order to achieve the maximum oil recovery in a given oil reservoir, it is important to determine an optimum timing for starting CO₂-EOR after waterflooding by considering the changed fluid saturations and complicated reservoir conditions. Obviously, a large extent of waterflooding will trap a large amount of the residual oil in the reservoir, which is difficult to recover in the subsequent CO₂-EOR process. On the other hand, water helps the oil recovery of CO₂ flooding because it reduces the mobility ratio between the displacing and displaced fluids and thus controls CO₂ viscous fingering [Juanes and Blunt, 2007]. In a water-alternating-gas (WAG) process, the injected water increases the sweeping efficiencies of the displacing fluids [Kulkarni and Rao, 2005]. In a carbonated water injection (CWI) process, water is also used to increase the sweeping efficiency of the displacing fluid [Kechut et al., 2011]. In consideration of the adverse and beneficial effects of the initial waterflooding on the subsequent CO₂ flooding, it is of fundamental and practical importance to determine the optimum extent of waterflooding before miscible CO₂ tertiary flooding is commenced.

1.3 Soaking Effect on Miscible CO₂ Flooding

Although CO₂-EOR can outperform the other EOR methods, it can only recover up to 12–25% of the original-oil-in-place (OOIP) in its actual field-scale applications [Pyo et al., 2003]. A more efficient CO₂-EOR process is still required to further increase the oil RF and subsequently store more greenhouse gas in the depleted oil reservoirs [Godec et al., 2013]. A modified CO₂-EOR method, namely CO₂ soaking-alternating-gas (CO₂-SAG) injection, has recently drawn some attention of the petroleum industry [Murray,
In CO₂-SAG injection, the miscible/immiscible displacement process in continuous CO₂ flooding and the CO₂-soaking process in CO₂ huff-n-puff are combined and conducted alternately. More specifically, in the first CO₂-flooding period, CO₂ is injected continuously into the oil reservoir to displace and recover the residual oil. In the subsequent CO₂-soaking period, both the injector and producer are closed so that the injected CO₂ diffuses into the residual reservoir fluids that are not touched by CO₂ yet. As the CO₂ concentration in the residual oil increases, the oil volume increases considerably but the oil viscosity decreases dramatically [Srivastava et al., 2000]. Meanwhile, the CO₂ concentration in the reservoir brine increases so that the IFT between the CO₂-saturated residual oil and carbonated reservoir brine is considerably reduced to overcome the waterblocking effect [Yang et al., 2005]. Moreover, the concentrations of extracted light-HCs in CO₂ increase in the CO₂-soaking period due to strong light-HCs extraction ability of supercritical CO₂. In the second CO₂-flooding period, CO₂ is injected again continuously to further displace and recover the CO₂-saturated residual oil.

In comparison with the other CO₂-EOR processes, CO₂-SAG injection has some obvious technical merits. First, CO₂ sweeps more areas of an oil reservoir in the two continuous CO₂-flooding periods, which leads to a much higher sweeping efficiency in comparison with that of CO₂ injection in CO₂ huff-n-puff process. Solvent convective dispersion between the injector and producer in the CO₂-SAG process results in a much higher oil RF than that in the solvent molecular diffusion in CO₂ huff-n-puff process. Second, CO₂ has a much longer retention time to fully interact with and completely saturate the residual oil and reservoir brine during the CO₂-soaking period of CO₂-SAG.
process. The CO$_2$-saturated light oil viscosity is dramatically reduced so as to achieve a much lower mobility ratio of the displacing CO$_2$ to the displaced oil. Hence, CO$_2$ sweeping efficiency in the second continuous CO$_2$-flooding period is substantially increased. Also due to CO$_2$ soaking, the oil swells and enters the previous CO$_2$ flowing channels to increase the oil recovery. Third, if pre-waterflooding is applied prior to the first continuous CO$_2$ flooding, the pre-waterflooding and the first continuous CO$_2$ flooding will be similar to the first cycle of a typical WAG injection to effectively control the mobility of the injected CO$_2$ [Li and Gu, 2014b]. Although CO$_2$-SAG injection has the above-mentioned technical advantages, few laboratory tests have been conducted to study this modified CO$_2$-EOR process and explore its actual potential to recover the light crude oil from a tight sandstone formation, such as the Pembina Cardium formation.

1.4 Mutual Interactions between the Reservoir Fluids and CO$_2$

The mutual interactions between the reservoir fluids (i.e., the residual oil and reservoir brine) and the injected CO$_2$ play an important role in the CO$_2$ tertiary flooding process, which include CO$_2$ dissolution, interfacial mass transfer, IFT reduction, and wettability alteration. It is well known that CO$_2$ dissolution into a light oil changes its properties, such as the oil viscosity reduction and oil-swelling effect [Srivastava et al., 2000]. In order to interact with the residual oil trapped by the reservoir brine, CO$_2$ has to dissolve first into the latter and then into the former [Grogan and Pinczewski, 1987]. The solvent interfacial mass transfer occurs through molecular diffusion due to solvent concentration distribution in the reservoir fluids and possibly through convective dispersion due to reservoir fluid flow in the porous media [Grogan et al., 1988]. The IFT
affects the CO₂-EOR process because it governs the fluid saturations in the oil reservoir [Yang et al., 2005]. A low or near-zero IFT between the light oil and the injected CO₂ leads to the multi-contact miscibility (MCM) development and thus a high miscible displacement efficiency. In a tight oil formation, a high capillary pressure due to a high IFT between the reservoir brine and the injected CO₂ prevents CO₂ from entering the small pores that are often occupied by water and thus blocks the mutual interactions between the residual oil surrounded by the reservoir brine and the injected CO₂. The wettability alteration of the rock surface may occur after it is in contact with the injected CO₂ and affect the CO₂-EOR process [Yang and Gu, 2008].

1.5 Purpose and Scope of this Thesis Study

The primary purpose of this thesis study is to determine the optimum timing for conducting miscible CO₂-EOR after waterflooding and study CO₂-soaking effect on miscible CO₂ flooding in a tight sandstone formation. The specific research objectives of this thesis are listed as follows:

1. To perform PVT tests and measure the saturation pressure ($P_{\text{sat}}$), oil-swelling factor (SF), gas–oil ratio (GOR) of CO₂-saturated light oil, and gas–water ratio (GWR) of CO₂-saturated reservoir brine;

2. To conduct viscosity measurements of CO₂-saturated light oils by using a capillary viscometer;

3. To measure the equilibrium IFTs between light oil/reservoir brine and CO₂, and determine the minimum miscibility pressure (MMP) between the light oil and CO₂ by using the vanishing interfacial tension (VIT) technique;
4. To conduct a series of miscible CO₂ coreflood tests after different extents of waterflooding and analyze the pore volume (PV) of CO₂ BT, oil RF of CO₂ flooding in terms of the residual-oil-in-place (ROIP), and total oil RF of waterflooding and CO₂ flooding; and

5. To undertake a series of miscible CO₂ coreflood tests with/without CO₂ soaking and examine the oil RF achieved in the second PV of CO₂ flooding and total oil RF of waterflooding and CO₂ flooding.

1.6 Outline of the Thesis

This Thesis is composed of five chapters. More specifically, Chapter 1 is an introduction to the thesis topic together with the purpose and scope of this thesis. Chapter 2 provides an up-to-date literature review on CO₂-EOR processes, CO₂ mobility control, waterblocking effect, and mutual interactions between the light oil and CO₂. This chapter also includes the problem statement of this thesis. Chapter 3 describes the experimental setups and experimental procedures for PVT tests, viscosity measurements, IFT tests, and coreflood tests. Chapter 4 discusses the PVT studies of the light oil/reservoir brine–CO₂ systems, viscosities of CO₂-saturated light oils, and IFT test results. The optimum timing for conducting miscible CO₂-EOR after waterflooding is determined and the soaking effect on miscible CO₂ flooding in a tight sandstone formation is examined. Chapter 5 summarizes some major scientific findings of this study and makes several technical recommendations for future studies.
CHAPTER 2  LITERATURE REVIEW

2.1  CO₂-EOR Methods

Since the 1950s, several different CO₂-EOR processes have been experimentally or numerically studied, pilot tested, and commercially applied in the oilfields. Among the major CO₂-EOR processes are continuous CO₂ flooding, CO₂-WAG injection, carbonated waterflooding, and CO₂ huff-n-puff process. Each CO₂-EOR process has its own technical advantages and disadvantages, which should be considered before it is applied in an oilfield. Continuous CO₂ flooding can achieve a high displacement efficiency but have a low sweeping efficiency. The high displacement efficiency is attributed to the strong mutual interactions between the crude oil and the injected CO₂ at the actual reservoir conditions [Nobakht et al., 2008]. In some idealized laboratory tests, for example, continuous miscible CO₂ secondary flooding in the slim-tube tests can achieve an oil RF of 80–95% [Dong et al., 2001]. However, the slim-tube test is conducted in a coiled long and small stainless steel tubing packed with small glass beads or Ottawa sands. This test does not take accounts of the reservoir heterogeneity, gravity effect, and viscous fingering due to an unfavourable mobility ratio of the displacing CO₂ to the displaced oil [Green and Willhite, 1998]. The major technical challenge of continuous CO₂ flooding in the oilfield applications is how to effectively minimize the mobility contrast [Stephenson et al., 1993] and the gravity overriding of the injected CO₂, which are attributed to its extremely low viscosity and relatively low density at the actual reservoir conditions, respectively.

CO₂-WAG injection combines the high displacement efficiency of the injected CO₂ and a relatively high sweeping efficiency of the injected water to jointly increase the
total oil RF. The overall performance of WAG injection is affected by the reservoir characteristics, well spacing, and injection strategy in the field applications [Christensen, et al., 2001]. For a specific oilfield, the operating parameters such as slug size, slug ratio, and cycle number can be optimized to maximize the ultimate oil RF of a CO₂-WAG injection [Chen et al., 2010]. Adding chemicals (surfactant, alkali, and polymer) into water can further enhance the oil RF of CO₂-WAG injection [Luo et al., 2013]. Moreover, water and gas can be co-injected, which is referred to as simultaneous water-alternating-gas (SWAG). Nevertheless, a large amount of the residual oil will be trapped in the oil reservoir and surrounded by an excessive amount of the injected water, and thus becomes difficult to access and recover, which is referred to as waterblocking effect [Grogan and Pinczewski, 1987]. Besides, gravity segregation also needs to be addressed during CO₂-WAG injection, which is caused by the density difference between the injected water and CO₂. The technical feasibility of CO₂-WAG injection is also questionable in a tight oil formation as the water injectivity is low in a low-permeability reservoir [Wang et al., 2010a].

Similarly, carbonated waterflooding also combines the technical advantages of waterflooding and CO₂ flooding together by dissolving CO₂ into water prior to its injection. The carbonated water is injected as a single-phase fluid, and thus its mobility is more favourable than continuous CO₂ flooding [Kechut et al., 2011]. Experimental results showed that it achieved a higher oil RF than conventional waterflooding due to the beneficial effect of the dissolved CO₂ [Sohrabi et al., 2012]. The first commercial application of carbonated waterflooding was conducted on the K&S project in the early 1960s [Hickok et al., 1960]. Nevertheless, the field application of carbonated
waterflooding is limited. Its actual performance is compromised because of a relatively low solubility of CO\textsubscript{2} in water and also a low injectivity of carbonated water in a tight oil formation.

Lastly, CO\textsubscript{2} huff-n-puff process is a special CO\textsubscript{2}-EOR method that is applied in a single vertical/horizontal well if this well has poor connectivities with the adjacent wells [Zhang et al., 2006]. The earliest CO\textsubscript{2} huff-n-puff projects were conducted by Texaco during the 1960s in California and Louisiana [Palmer et al., 1986]. The huff-n-puff process consists of three distinct periods: solvent injection, solvent soaking, and oil production periods, and thus is also called cyclic solvent injection (CSI) or process (CSP) [Torabi and Asghari, 2010]. Its major EOR mechanism relies on the solvent molecular diffusion rather than the solvent convective dispersion (i.e., miscible/immiscible displacement). Thus the ultimate contact or drainage area of the injected CO\textsubscript{2} is relatively small in a typical CO\textsubscript{2} huff-n-puff process.

### 2.2 CO\textsubscript{2} Mobility Control

The major technical challenge of continuous CO\textsubscript{2} flooding is the high mobility of CO\textsubscript{2} due to its extremely low viscosity. A typical viscosity of CO\textsubscript{2} is around 0.04 mPa·s under the reservoir conditions, which is much lower than the light crude oil viscosity [Li and Gu, 2014a]. Early CO\textsubscript{2} BT and gas channeling usually happen and become more severe in a highly heterogeneous reservoir. Several methods have been developed to control the mobility of CO\textsubscript{2}, including CO\textsubscript{2}-WAG injection, thickening CO\textsubscript{2} by using a polymer as a direct thickener, and CO\textsubscript{2}-foaming injection. CO\textsubscript{2}-WAG is the most commonly used method in oilfields to control the mobility of CO\textsubscript{2} by injecting water and CO\textsubscript{2} slugs alternately. Caudle and Dyes [1957] first proposed to inject water and gas
together to control the mobility of the injected gas in 1957, which was developed into WAG injection later. The gas saturation is reduced by the injected water and thus the gas relative permeability is reduced. The performance of WAG injection is affected by several factors. It was reported that the rock wettability would affect the oil RF of WAG injection [Fatem and Sohrabi, 2013]. The injected gas composition will also affect the performance of WAG injection [Bermudez et al., 2007]. In addition, the effects of well configuration, WAG ratio, cycle length, and timing of WAG process have been studied by applying numerical simulation [Wu et al., 2004]. A typical oil RF of WAG injection is in the range of 5–10% in the oilfield application, which means that there is still a large potential to further optimize the WAG injection [Christensen et al., 2001].

Thickening CO₂ by using polymer is another method to control the mobility of CO₂. The viscosity of the displacing phase is increased by dissolving a polymer into it and thus the mobility of the displacing phase is reduced. It was reported that the viscosity of CO₂ was increased by approximately 14 times by dissolving a polymer thickener into it [Zhang et al., 2011]. Coreflood test results showed that gas BT was significantly delayed with the injection of polymer-thickened CO₂ in comparison with pure CO₂ flooding, which indicated a better mobility control of polymer-thickened CO₂ [Bae and Irani, 1993]. There are two methods to increase the viscosity of CO₂: one is to add cosolvents that help polymer to dissolve into CO₂. Another method is to dissolve polymers into CO₂ directly without cosolvents [Rousseau et al., 2012]. The first method has been studied by Davis [1992]. It was found that a mixture of CO₂, polysilylenesiloxane, and cosolvents increased the viscosity of CO₂ by at least three folds. The suitable cosolvents can be alcohol, aromatics, or kerosene. However, large
amounts of required cosolvents limit their economic feasibilities for field applications. The viscosity enhancement mechanism of the second method is that the CO$_2$-philic groups of the polymer enhance the solubility of polymer in CO$_2$ and the CO$_2$-phobic groups of the polymer promote intermolecular associations to increase the viscosity [Enick et al., 2000]. Numerous laboratory studies, including solubility tests and viscosity measurements, have been conducted to find suitable polymers. Several technical issues need to be addressed before polymer-thickened CO$_2$ can be applied in an oil reservoir. Some polymers may adsorb onto the surface of the pores and throats and cause severe permeability reduction in the reservoir [Rousseau et al., 2012]. Polymers may also degrade due to a high shear stress during the injection process. The future research of thickening CO$_2$ by using polymer is to find cost-effective and environment-friendly polymers with high solubilities in CO$_2$ and strong capabilities to increase CO$_2$ viscosity.

Injecting CO$_2$-foam is also effective to control the mobility of the displacing phase (i.e., CO$_2$). CO$_2$-foam is generated by mixing CO$_2$ with a surfactant solution. Inside foam, gas bubbles are surrounded by thin liquid films (TLFs) and dispersed in the mixture. The surface tension on the TLFs and drag force along the pore surface will cause resistance to movement when foam flows through the porous media, resulting in an increased apparent gas viscosity. The mobility and stability of CO$_2$-foam are affected by several factors, such as foam quality, operating pressure, brine salinity, oil properties, and surfactant properties [Farzaneh and Sohrabi, 2013]. Foam quality is defined as the ratio of gas injection rate to the total injection rate. CO$_2$-foam flooding will be effective only when foam quality is in a suitable range [Chang and Grigg, 1999]. A high
operating pressure will help to improve the foam stability and oil recovery performance of CO₂-foam flooding [Chang et al., 1994]. A high salinity usually leads to a low solubility of a surfactant in the brine and thus destabilizes CO₂-foam. It was found that oil was generally detrimental to the stability of foam [Schramm, 1992]. The surfactant plays a vital role in CO₂-foam flooding and an appropriate surfactant should be able to stabilize the foam and avoid excessive adsorption onto the surface of the pores and throats [Farzaneh and Sohrabi, 2013]. Developing more cost-effective surfactants is the key technical challenge to the successful application of CO₂-foam flooding in an oilfield.

### 2.3 Waterblocking Effect

In oilfield applications, CO₂ flooding is usually conducted as a tertiary flooding process to recover the residual oil after waterflooding. The residual oil can be divided into two parts: the first part in the area untouched by water; and the other part in the area touched by water [Stalkup, 1970]. The residual oil in the area flooded by water is trapped by the injected water, which is referred to as waterblocking effect [Bijeljic et al., 2002]. A dead end pore model is usually used to describe the oil recovery process of the water-trapped residual oil, which is shown in Figure 1.1. The injected solvent (e.g., CO₂) must displace the excessive amount of water in the flowing channel first, and then dissolve into water film, and finally interact with the water-trapped residual oil. The water-trapped residual oil will swell, displace the water barrier, contact directly with the injected CO₂, and finally be recovered [Campbell and Orr, 1985]. This process is mainly a molecular diffusion process and depends on the diffusion coefficient of CO₂ in the water/oil, CO₂ partition coefficient between the oil and water, solubilities of CO₂ in the water and oil, and contact time between the reservoir fluids and CO₂.
Figure 1.1  Schematic diagram of the dead end pore model [Campbell and Orr, 1985].
A high diffusion coefficient of CO₂ in the water/oil means a high mass-transfer rate of CO₂ in the water/oil and will help to quickly recover the water-trapped residual oil [Muller and Lake, 1991]. Several methods have been developed to measure the diffusion coefficient of CO₂ in the water/oil. The pressure decay method (PDM) has been used to measure the diffusion coefficients of different solvents including CO₂ in the crude oil [Tharanivasan et al., 2004]. Another method named dynamic pendant drop volume analysis (DPDVA) was developed to measure diffusion coefficient of CO₂ in the crude oil [Yang and Gu, 2005]. In addition, the diffusion coefficient of CO₂ in the crude oil can also be determined by analyzing the dynamic IFT [Yang et al., 2006]. The diffusion coefficient of CO₂ in the water has been measured by many researchers. A typical diffusion coefficient of CO₂ in the pure water is $3.6 \times 10^{-9}$ m²/s at the reservoir condition of 13.1 MPa and 54 °C [Grogan and Pinczewski, 1987].

The CO₂ partition coefficient is an important parameter in CO₂ molecular diffusion from water to oil, which is defined as the ratio of mass fraction of CO₂ in the oil phase to the mass fraction of CO₂ in the water phase at the equilibrium state [Peksa et al., 2013]. The CO₂ partition coefficient varies with the oil–water system. The solubility of CO₂ in oil/water can be measured by using a PVT system and a large number of experimental tests have been conducted to determine the solubility of CO₂ in oil/water. A sufficient contact time is the key parameter to recover the residual oil from dead end pores, due to the slow diffusion process with small diffusion coefficients of CO₂ in water and oil. Unlike the well established dead end pore model, it is more challenging to recover the water-trapped residual oil from porous media. Oil drop size and distribution of the water-trapped residual oil, pore size, pore structure, and wettability of the porous
media vary with the location in core plugs and reservoir [Chatzis et al., 1983]. In coreflood tests, the contact time or retention time is defined as the ratio of core length to the average linear velocity of injection solvent. Assumed mean lengths of oil drops and shielding water phase were used to study the waterblocking effect in coreflood tests and estimate the reasonable contact time for recovering the water-trapped residual oil. It was found that a longer contact time was needed for a given oil drop to be recovered when the water barrier was thick [Grogan and Pinczewski, 1987]. A sufficient contact time can be achieved by reducing CO$_2$ injection rate or conducting soaking process [Tiffin and Yellig, 1983]. The diffusion of CO$_2$ into the water-trapped residual oil will take 8–80 years as the scale of bypassing and waterblocking is much larger in a field-scale application [Grogan and Pinczewski, 1987].

2.4 Mutual Interactions between the Light Oil and CO$_2$

The study of mutual interactions between the light oil and CO$_2$ is vital before a CO$_2$-EOR project is conducted. Strong mutual interactions will happen when CO$_2$ contacts the light oil, which include asphaltene precipitation, oil-swelling and light-HCs extraction, IFT reduction and miscibility development, and viscosity reduction. The asphaltenes may become unstable and precipitate when CO$_2$ is dissolved into a crude oil. Although the asphaltene content in light oil is usually low, asphaltenes will still cause severe problems as the permeability of a light oil reservoir is usually low. For example, the Hassi–Messaould field with an asphaltene content of 0.15 wt.% in its light crude oil had severe asphaltene precipitation problems [Sarma, 2003]. The onset CO$_2$ concentration in a Weyburn light oil–CO$_2$ system for asphaltene precipitation was determined by using a PVT system [Srivastava et al., 1999]. The onset pressure of
asphaltene precipitation in a Pembina Cardium light oil–CO₂ system was determined by applying a visualization method in a saturation cell [Wang and Gu, 2011]. New inhibitors have been developed to prevent the asphaltene precipitation, not only in the production tubing, but also within the reservoir [Leonard et al., 2013].

Strong oil-swelling and light-HCs extraction happen due to strong two-way mass-transfer between the light oil and CO₂. A high-pressure IFT cell has been used to observe and study these two phenomena between the light oil and CO₂ by introducing an oil drop into a high-pressure cell filled with CO₂ [Gu et al., 2013]. It was found that the oil drop volume increased at the beginning and then reduced gradually when the pressure is lower than the initial strong light-HCs extraction pressure. Quick light-HCs extraction was found once oil drop was introduced into the high-pressure IFT cell when pressure was higher than the initial strong light-HCs extraction pressure [Wang et al., 2010b]. Another method was used to study the oil-swelling and light-HCs extraction effects by introducing suitable amounts of light oil and CO₂ into a PVT cell and measuring the oil SF. The oil SF always increased with the equilibrium pressure and CO₂ solubility when the pressure was below the pressure of extraction point. The oil SF started to decrease when the equilibrium pressure and CO₂ solubility reached certain levels [Tsau et al., 2010].

The IFT between the light oil and CO₂ will directly affect the capillary number and displacement efficiency [Nobakht et al., 2008]. The dynamic IFT between the light crude oil and CO₂ will be reduced gradually and finally reached the equilibrium IFT at a given pressure and temperature [Yang et al., 2005]. The equilibrium IFT between the light crude oil and CO₂ reduces with the increased pressure at a specified temperature
[Gu et al., 2013]. The equilibrium IFT versus pressure data can be used to determine the MMP by applying the VIT technique, which is defined as the minimum pressure for light oil and solvent to become miscible through multiple contacts [Rao and Lee, 2002]. Others experimental methods, such as slim-tube tests, rising bubble apparatus (RBA), can also be used to determine the MMP.

The crude oil viscosity will decrease significantly with the dissolution of CO$_2$. Thus the mobility contrast between the displacing CO$_2$ and displaced oil will be reduced and both the displacement efficiency and sweeping efficiency will increase. It was reported that a CO$_2$-saturated Weyburn crude oil viscosity was decreased from 3.01 to 0.20 mPa·s when CO$_2$ concentration increased from 0.58 to 82.6 mol.% [Srivastava et al., 2000]. A high-pressure capillary viscometer or a high-pressure rolling-ball viscometer is usually used to measure the CO$_2$-saturated oil viscosity.

### 2.5 Problem Statement

As described in the preceding sections of this chapter, the viscous fingering and waterblocking effect need to be studied before a CO$_2$ flooding process is applied, especially CO$_2$ tertiary flooding. Thus it is of importance to find the optimum timing for conducting CO$_2$ flooding after waterflooding. Also the mutual interactions (including the contact time) between the light oil and CO$_2$ are not strong enough during a continuous CO$_2$ flooding process. Thus it is meaningful to elongate the contact time by applying soaking to enhance oil recovery from tight oil formations. In the literature, limited research has been done to study the effects of timing and soaking on CO$_2$ flooding. Therefore, the main objective of this thesis is to optimize the CO$_2$
secondary/tertiary process by finding the optimum timing for conducting CO₂-EOR and applying CO₂-soaking process.

In this study, the mutual interactions between light oil/reservoir brine and CO₂, optimum timing for miscible CO₂-EOR after waterflooding, and soaking effect on miscible CO₂ flooding in a tight sandstone formation were studied. First, the $P_{\text{sat}}$, oil SF, and GOR of CO₂-saturated light oil, and GWR of CO₂-saturated brine were measured by using a PVT system. Second, the viscosities of CO₂-saturated light oil with different CO₂ concentrations were measured by using a capillary viscometer. Third, the equilibrium IFTs between the light oil/reservoir brine and CO₂ were measured at different equilibrium pressures and the actual reservoir temperature by applying the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. Finally, five coreflood tests were undertaken to determine the optimum timing for miscible CO₂-EOR after waterflooding and six coreflood tests were performed to examine CO₂-soaking effect on miscible CO₂ flooding in a tight sandstone formation, respectively.
CHAPTER 3  EXPERIMENTAL

3.1 Materials

The original light oil was collected from the Pembina Cardium formation in Alberta, Canada. The obtained light oil was cleaned by using a centrifuge (Allegra X-30 Series, Beckman Coulter, USA) to remove any sands and brine. Also an inline filter (SS-2TF-0.5, Swagelok, Canada) with a pore size of 0.5 μm was used to further remove any fine solids from the light oil. The density and viscosity of the cleaned light oil were measured to be 0.847 g/cm$^3$ and 10.30 cP at the atmospheric pressure and $T_{\text{lab}} = 22.0 \, ^{\circ}\text{C}$; 0.827 g/cm$^3$ and 6.27 cP at the atmospheric pressure and $T_{\text{res}} = 53.0 \, ^{\circ}\text{C}$ by using a densitometer (DMA 512P, Anton Paar, USA) and a viscometer (DV-II+, Brookfield, USA), respectively. The molecular weight of the light oil was measured to be 225.0 g/mol by using an automatic high-sensitivity wide-range cryoscopy (Model 5009, Precision Systems Inc., USA), which was conducted by the Core Laboratories. The asphaltene content of the light oil was measured to be $w_{\text{asp}} = 0.48 \, \text{wt.\% (n-pentane insoluble)}$ by using the standard ASTM D2007-03 method [2007] and filter papers (No. 5, Whatman, England) with a pore size of 2.5 μm. The composition analysis of the cleaned light oil was obtained by using the standard ASTM D86 method [2003] and conducted by the Saskatchewan Research Council. Its detailed result is given in Table 3.1. As the light oil is dead oil with no dissolved solution gas, it does not have methane, ethane, and propane. The total mole percentage of $C_{1-10}$ is 38.23 mol.% and the total mole percentage of $C_{50+}$ is equal to 4.02 mol.%. These data indicate that the light crude oil contains a large amount of light to intermediate hydrocarbons and is especially
Table 3.1  Compositional analysis result of the cleaned Pembina Cardium original light oil ($\rho_{oil} = 0.827$ g/cm$^3$ and $\mu_{oil} = 6.27$ mPa·s at the atmospheric pressure and $T_{res} = 53.0$ °C, $MW_{oil} = 225.0$ g/mol) with the asphaltene content of $w_{asp} = 0.48$ wt.% ($n$-pentane insoluble).

<table>
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<th>carbon no.</th>
<th>mol.%</th>
<th>carbon no.</th>
<th>mol.%</th>
</tr>
</thead>
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</tr>
<tr>
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<td>0.00</td>
<td>C28</td>
<td>1.09</td>
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<tr>
<td>C3</td>
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</tr>
<tr>
<td>C4</td>
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<td>C35</td>
<td>0.59</td>
</tr>
<tr>
<td>C10</td>
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</tr>
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<td>C11</td>
<td>5.65</td>
<td>C37</td>
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</tr>
<tr>
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<td>C38</td>
<td>0.35</td>
</tr>
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<td>0.49</td>
</tr>
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<td>C40</td>
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<td>0.18</td>
</tr>
<tr>
<td>C23</td>
<td>1.51</td>
<td>C49</td>
<td>0.17</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>C26</td>
<td>1.23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
suitable for CO$_2$-EOR.

The reservoir brine sample was also collected from the same formation and cleaned by using the same inline filter to remove any fine solids. Its detailed physicochemical properties were analyzed by the Saskatchewan Research Council and are listed in Table 3.2. The concentration of its total dissolved solids (TDS) is equal to 4,230 mg/L at 180 °C. The dominant cation is sodium and the dominant anion is chlorine. A number of tight sandstone reservoir core plugs were collected from several wells located in the Pembina Cardium formation at the reservoir depths of 1,600–1,648 m. The purity of carbon dioxide (Praxair, Canada) used in this study was equal to 99.998 mol.%. The densities of pure CO$_2$ at different pressures and temperatures were calculated by using the CMG WinProp module (Version 2011.10, Computer Modelling Group Limited, Canada) with Peng–Robinson equation of state (P–R EOS) [Peng and Robison, 1976].

3.2 Saturation Pressure Measurements

A DBR PVT system (PVT-0150-100-200-316-155, DBR, Canada) was used to measure the saturation pressures of CO$_2$-saturated light oils with different CO$_2$ concentrations at $T_{\text{res}} = 53.0$ °C. A schematic diagram of the DBR PVT system is shown in Figure 3.1. The key component of this system was a visual PVT cell, where fluid samples were encapsulated inside a glass tube. The maximum sample volume of this glass tube was 130 cm$^3$. Inside the glass tube, a movable piston was used to separate the test fluids from the surrounding hydraulic oil. The maximum operating pressure and temperature of the PVT system were equal to 68 MPa and 200 °C. The test pressure of the PVT cell was adjusted by using an automatic positive-displacement pump (PMP-
Table 3.2  Physical and chemical properties of the cleaned Pembina Cardium reservoir brine at $P = 1$ atm.

<table>
<thead>
<tr>
<th>Property</th>
<th>15</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature (°C)</td>
<td>15</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>density (g/cm³)</td>
<td>1.003</td>
<td>1.002</td>
<td>0.996</td>
</tr>
<tr>
<td>viscosity (mPa·s)</td>
<td>1.17</td>
<td>1.02</td>
<td>0.66</td>
</tr>
<tr>
<td>pH at 20.0 °C</td>
<td>8.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>specific conductivity (μS·cm⁻¹)</td>
<td>6,860</td>
<td></td>
<td></td>
</tr>
<tr>
<td>refractive index at 25.0 °C</td>
<td>1.3334</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chloride (mg/L)</td>
<td>1,480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulphate (mg/L)</td>
<td>9.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total dissolved solids (mg/L)</td>
<td>4,230 at 180 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>potassium (mg/L)</td>
<td>8.8</td>
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<tr>
<td>sodium (mg/L)</td>
<td>1,680</td>
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<td></td>
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<tr>
<td>calcium (mg/L)</td>
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</tr>
<tr>
<td>magnesium (mg/L)</td>
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<tr>
<td>iron (mg/L)</td>
<td>0.098</td>
<td></td>
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</tr>
<tr>
<td>manganese (mg/L)</td>
<td>0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>barium (mg/L)</td>
<td>5.5</td>
<td></td>
<td></td>
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</tbody>
</table>
Figure 3.1  Schematic diagram of the DBR PVT system.
-1-10-MB-316-M4-C0, DBR, Canada) to move the piston upward or downward. A magnetic stirrer was used to mix the test fluids inside the glass tube. A video-based digital cathetometer with a resolution of 0.0025 cm was used to measure the phase heights/volumes. The test temperature was maintained by using an airbath within ± 0.1 °C. The test pressure was measured by using a digital pressure indicator (Model 901A, Heise, USA) with an accuracy of 7 psi. The PVT cell and three respective sample cylinders filled with the light oil, brine, and pure CO₂ were kept inside the airbath.

Prior to each PVT test, the PVT cell and the fluids handling system were thoroughly cleaned with kerosene, flushed with nitrogen for several times, and finally vacuumed to remove any traces of the cleaning agents. The test temperature of the airbath was first set at $T_{\text{lab}} = 22.0 \, ^\circ\text{C}$ 24 h before each PVT test so that the fluid sample cylinders and the PVT cell would reach the pre-specified reservoir temperature at a later time. To measure the saturation pressure ($P_{\text{sat}}$) of CO₂-saturated light oil, first, the PVT cell was filled with CO₂ in a gaseous phase at an initial pressure below its vapour pressure at the laboratory temperature. The mass of CO₂ was determined by multiplying its predicted density from the P–R EOS modeling and measured volume. Second, the light crude oil was injected into the PVT cell. The volume of the injected light oil was determined by subtracting the predicted volume of CO₂ from the P–R EOS modeling at an increased actual pressure from the measured total volume of the light oil–CO₂ mixture immediately after the oil injection. It was assumed that there was no CO₂ dissolution into the light oil at the very beginning of mixing. Third, the test temperature of the PVT cell was gradually increased to and maintained at $T_{\text{res}} = 53.0 \, ^\circ\text{C}$ by using an airbath for 12 h, while the magnetic stirrer was turned on to vigorously mix the light oil and CO₂. Finally, the continuous
depressurization method with a constant withdrawal rate of 3 cm$^3$/h was used to determine the saturation pressure of the light oil–CO$_2$ mixture at $T_{\text{res}} = 53.0$ °C.

After each PVT test was completed, the curve of the light oil–CO$_2$ mixture pressure ($P_{\text{cell}}$) in the PVT cell versus the specific volume ($v_{\text{mix}}$) was plotted. The sudden change point of the slope of $P_{\text{cell}}$ versus $v_{\text{mix}}$ curve was defined to be the saturation point, at which there was only one phase in the PVT cell as CO$_2$ was completely dissolved into the light oil. Here, $v_{\text{mix}}$ denotes the mass-based specific volume of the light oil–CO$_2$ system at a given $P_{\text{cell}}$ and $T_{\text{res}}$:

$$v_{\text{mix}} (P_{\text{cell}}, T_{\text{res}}) = \frac{V_{\text{mix}} (P_{\text{cell}}, T_{\text{res}})}{m_{\text{mix}}},$$

(3.1)

where, $V_{\text{mix}}$ and $m_{\text{mix}}$ (i.e., $m_{\text{oil}} + m_{\text{CO}_2}$) represent the measured total volume and mass of the light oil–CO$_2$ mixture. The pressure at the saturation point was called the saturation pressure ($P_{\text{sat}}$) of CO$_2$-saturated light oil.

### 3.3 Oil-Swelling Factor Measurements

Accordingly, the oil SF of CO$_2$-saturated light oil was defined as:

$$SF (P_{\text{sat}}, T_{\text{res}}) = \frac{V_{\text{mix}} (P_{\text{sat}}, T_{\text{res}})}{V_{\text{oil}} (1 \text{ atm}, T_{\text{res}})},$$

(3.2)

where, $V_{\text{mix}}$ is the measured total volume of CO$_2$-saturated light oil at the saturation pressure and reservoir temperature of $T_{\text{res}} = 53.0$ °C and $V_{\text{oil}}$ is the measured volume of the dead light oil at the atmospheric pressure and reservoir temperature of $T_{\text{res}} = 53.0$ °C.
3.4 GOR Measurements

After the saturation point is determined, the GOR of CO$_2$-saturated light oil at the saturation pressure and reservoir temperature is equal to:

\[
GOR(P_{\text{sat}}, T_{\text{res}}) = \frac{m_{\text{CO}_2} / \rho_{\text{CO}_2}}{m_{\text{oil}} / \rho_{\text{oil}}}_{\text{sc}} = \frac{V_{\text{CO}_2}}{V_{\text{oil}}}_{\text{sc}},
\]

(3.3)

where, \(m_{\text{CO}_2}\) is the mass of CO$_2$; \(\rho_{\text{CO}_2}\) and \(V_{\text{CO}_2}\) are the density and volume of CO$_2$ at the standard conditions (i.e., \(P_{\text{sc}} = 1\) atm and \(T_{\text{sc}} = 15.6\) °C); \(m_{\text{oil}}\) is the mass of the dead light oil; \(\rho_{\text{oil}}\) and \(V_{\text{oil}}\) denote the density and volume of the dead light oil with no CO$_2$ dissolution at the standard conditions.

In addition to the above-mentioned GOR measurement, a flashing method was also used to measure the GOR. A schematic diagram of the experimental setup used in the flashing method is also shown in Figure 3.1. First, a programmable syringe pump was used to apply a high pressure at the outlet of a back-pressure regulator (BPR-50, Temco, USA) until its outlet pressure was above the saturation pressure. The positive-displacement pump was used to displace the CO$_2$-saturated light oil through the back-pressure regulator. A quick separation of oil and gas took place after the CO$_2$-saturated light oil passed through the back-pressure regulator. The separated oil was collected inside a graduated glass tube, which functioned as a two-phase separator, and weighed by using a high-precision electronic balance (PR 210, Cole–Parmer, Canada). The flashed gas was collected in an air bubbler, where its volume was measured. The GOR of CO$_2$-saturated light oil at the saturation pressure and reservoir temperature was measured by using the above-mentioned flashing method:
\[
GOR (P_{\text{sat}}, T_{\text{sat}}) = \left[ \frac{\dot{V}_{\text{CO}_2} \times \rho'_{\text{CO}_2} / \rho_{\text{CO}_2}}{m_{\text{oil}} / \rho_{\text{oil}}} \right]_{\text{sc}},
\]

where, \( \rho_{\text{CO}_2} \) and \( \dot{V}_{\text{CO}_2} \) are the density and volume of \( \text{CO}_2 \) flashed from the \( \text{CO}_2 \)-saturated light oil at \( P_{\text{sc}} = 1 \text{ atm} \) and \( T_{\text{lab}} = 22.0 \text{ °C} \).

### 3.5 GWR Measurements

Unlike the light oil–\( \text{CO}_2 \) system, the reservoir brine–\( \text{CO}_2 \) system has an obvious interface between the upper free \( \text{CO}_2 \) phase and the lower \( \text{CO}_2 \)-saturated brine inside the PVT cell, which can be observed clearly. To measure the GWR of the \( \text{CO}_2 \)-saturated reservoir brine, first, the PVT cell was filled with \( \text{CO}_2 \) in a gaseous phase at an initial pressure below its saturation pressure and at the laboratory temperature. The initial mass of \( \text{CO}_2 \) was determined from its predicted density through the P–R EOS modeling and measured volume. Second, the reservoir brine was injected into the PVT cell and its volume was measured by using the digital cathetometer directly. The mass of the injected brine was determined from its measured density and volume. Third, the temperature of the PVT cell was gradually increased to and maintained at \( T_{\text{res}} = 53.0 \text{ °C} \) for 12 h by using the airbath, while the magnetic stirrer was turned on to vigorously mix the reservoir brine and \( \text{CO}_2 \). Lastly, the PVT cell pressure was increased by using the positive-displacement pump in order to measure the GWRs of the \( \text{CO}_2 \)-saturated reservoir brine at different equilibrium pressures. To reach each equilibrium pressure, the magnetic stirrer was turned on for several hours to fully mix the reservoir brine and \( \text{CO}_2 \) until their mixture reached its equilibrium state, which was indicated by a constant pressure in the PVT cell. The final mass of the upper free \( \text{CO}_2 \) phase (i.e., the gas cap)
was determined from its predicted density through the P–R EOS modeling and measured volume at the experimental conditions. The mass of CO₂ that dissolved into the brine was determined by subtracting the final mass of free CO₂ in the gas cap from the initial mass of CO₂ in the PVT cell at the beginning. Hence, the GWR of the CO₂-saturated reservoir brine at each equilibrium pressure and \( T_{res} = 53.0 \, ^\circ C \) is found to be:

\[
GWR(P_{eq}, T_{res}) = \frac{(m^i_{CO_2} - m^f_{CO_2}) / \rho_{CO_2}}{m_{brane} / \rho_{brane}} \bigg|_{sc},
\]

(3.5)

where, \( m^i_{CO_2} \) and \( m^f_{CO_2} \) represent the initial mass of CO₂ in the PVT cell at the beginning and the final mass of free CO₂ in the gas cap at the end; \( m_{brane} \) denotes the mass of the reservoir brine tested; and \( \rho_{brane} \) is the density of the reservoir brine at the standard conditions (i.e., \( P_{sc} = 1 \, \text{atm} \) and \( T_{sc} = 15.6 \, ^\circ C \)). In addition, the GWR \( (P_{eq}, T_{res}) \) was also predicted by using the CMG WinProp module, assuming that the reservoir brine were pure water with zero salinity.

3.6 Viscosity Measurements

To measure the viscosity of CO₂-saturated light oil at its saturation pressure and \( T_{res} = 53.0 \, ^\circ C \), a capillary viscometer was constructed and connected to the PVT cell inside the airbath. Its schematic diagram is shown in Figure 3.2. A 35-foot long stainless steel tubing (SS-T1-S-020-20, Swagelok, Canada) was coiled onto two specially designed cylinders. The outer diameter (OD) of the capillary tubing was 1/16 inch and its wall thickness was 0.02 inch. The total interior void volume of the capillary tubing was calculated to be 2.737 cm³. This long and small capillary tubing was chosen to ensure
Figure 3.2  Schematic diagram of the capillary viscometer used for measuring the viscosity ($\mu_{\text{mix}}$) of CO$_2$-saturated light oil.
that a pressure drop along it was large enough to accurately measure the low viscosity of CO₂-saturated light oil. A programmable syringe pump (100DX, ISCO Inc., USA) was used to apply a high pressure at the outlet of a back-pressure regulator (BPR-50, Temco, USA) until its outlet pressure was about 0.5 MPa above the saturation pressure \( P_{\text{sat}} \) to ensure that each CO₂-saturated light oil remained one liquid phase inside the capillary tubing during its viscosity measurement. The automatic positive-displacement pump was used to inject the CO₂-saturated light oil through the capillary viscometer. The injection rate was controlled by using the positive-displacement pump and three different constant volume flow rates \( q_{\text{mix}} = 0.1, 0.2, \) and 0.3 cm\(^3\)/min) were used. When the CO₂-saturated light oil passed through the capillary tubing, the pressures at its two ends were measured by using a digital pressure indicator (PM, Heise, USA) and recorded in a personal computer at a preset time interval of 1 s.

Prior to CO₂-saturated light oil viscosity measurements, a distilled water with \( \mu_w = 0.521 \) mPa·s at \( T_{\text{res}} = 53.0 \) °C was used as a standard viscosity liquid and injected through the capillary tubing at different constant volume flow rates \( q_w = 0.5-15.0 \) cm\(^3\)/min) to calibrate the capillary viscometer. The distilled water was chosen as its viscosity is close to the low viscosity of CO₂-saturated light oil under the actual reservoir conditions. Then the Poiseuille equation was applied to determine the so-called “effective radius” of the capillary tubing. With the determined “effective radius”, this equation was applied to determine the CO₂-saturated light oil viscosity:

\[
\mu_{\text{mix}} (P_{\text{sat}}, T_{\text{res}}) = \frac{\pi (r_{\text{eff}})^4 \Delta P}{8 q_{\text{mix}} L},
\]  

(3.6)
where, $\mu_{\text{mix}}$ is the viscosity of CO$_2$-saturated light oil at each saturation point; $\Delta P$ and $q_{\text{mix}}$ are the measured pressure drop and prespecified constant volume flow rate of the CO$_2$-saturated light oil through the capillary tubing; $r_{\text{eff}}$ and $L$ are the “effective radius” and the length of the capillary tubing, which are 0.00045 m and 10.668 m, respectively.

### 3.7 IFT Measurements

Figure 3.3 shows a schematic diagram of the experimental setup used for measuring the equilibrium IFT between the light oil/reservoir brine and CO$_2$ by applying the ADSA technique for the pendant drop case [Cheng et al., 1990]. The major component of this experimental setup was a see-through windowed high-pressure IFT cell (IFT-10, Temco, USA). A stainless steel syringe needle was installed at the top of the IFT cell and used to form a pendant liquid (light oil or reservoir brine) drop. The light oil/reservoir brine was introduced from a transfer cylinder (500-10-P-316-2, DBR, Canada) to the syringe needle by using a programmable syringe pump (100DX, ISCO Inc., USA). A light source and a glass diffuser were used to provide uniform illumination for the pendant liquid drop. A microscope camera (KPM1U, Hitachi, Japan) was used to capture the sequential digital images of the dynamic pendant liquid drops inside the IFT cell at different times. The high-pressure IFT cell was positioned horizontally between the light source and the microscope camera. The entire ADSA system and the high-pressure IFT cell were placed on a vibration-free table (RS4000, Newport, USA). The digital images of the dynamic pendant light oil or reservoir brine drops at different times were acquired in tagged image file format (TIFF) by using the digital frame grabber (Ultra II, Coreco Imaging, Canada) and stored in a DELL desktop computer.
Figure 3.3  Schematic diagram of the experimental setup used for measuring the equilibrium interfacial tension (IFT) between the light oil/reservoir brine and CO$_2$ by applying the axisymmetric drop shape analysis (ADSA) technique for the pendant oil drop case.
The high-pressure IFT cell was first filled with CO₂ at a prespecified pressure and a constant temperature. After the pressure and temperature inside the IFT cell reached their stable values, the light oil or reservoir brine sample was introduced from the high-pressure transfer cylinder to form a pendant liquid drop at the tip of the syringe needle. Once a well-shaped pendant liquid drop was formed, the sequential digital images of the dynamic pendant liquid drop at different times were acquired and stored automatically in the personal computer. Then the ADSA program for the pendant drop case was executed to determine the dynamic IFT of the pendant liquid drop surrounded by CO₂. In this study, the light oil–CO₂ dynamic and equilibrium IFTs were measured at twelve different equilibrium pressures of \( P_{eq} = 1.0 \text{–} 12.4 \text{ MPa} \) and the constant reservoir temperature of \( T_{res} = 53.0 \degree C \). In addition, the reservoir brine–CO₂ dynamic and equilibrium IFTs were measured at five different equilibrium pressures of \( P_{eq} = 1.0 \text{–} 12.0 \text{ MPa} \) and at the same reservoir temperature of \( T_{res} = 53.0 \degree C \).

### 3.8 Coreflood Tests

A schematic diagram of the coreflood apparatus used in the coreflood tests is shown in Figure 3.4. Prior to each test, the sandstone reservoir core plugs were cleaned by applying Dean–Stark extractor (09-55D, Fisher Scientific, Canada). The composite reservoir core plugs used in the five CO₂ coreflood tests were 6–7 inches long and 2 inches in diameter. An automatic displacement pump (PMP-1000-1-10-MB, DBR, Canada) was used to displace the light oil, reservoir brine or CO₂ through the composite reservoir core plugs inside a coreholder (RCHR-2.0, Temco, USA). The tap water was
Figure 3.4  Schematic diagram of the high-pressure CO₂ coreflood apparatus.
pumped by using the syringe pump to apply the so-called overburden pressure, which was always kept 5 MPa higher than the injection pressure (i.e., the inlet pressure). Four high-pressure transfer cylinders (500-10-P-316-2, DBR, Canada) were used to store and deliver the light oil, reservoir brine, CO₂, and tap water, respectively. These four transfer cylinders and the coreholder were placed inside an air bath. A heating gun (HG 1100, Thankita, USA) and a temperature controller (Standard-89000-00, Cole–Parmer, Canada) were used to heat the air bath and keep its constant temperature of $T_{\text{res}} = 53.0 \, ^\circ\text{C}$. The same back-pressure regulator (BPR-50, Temco, USA) was used to maintain the production pressure (i.e., the outlet pressure). During the original light oil, reservoir brine, and CO₂ injection processes, the injection and production pressures were measured by using a digital pressure indicator (PM, Heise, USA). The instantaneous gas flow rate and cumulative gas production from the outlet of the coreholder were measured every second by using a gas flow meter (XFM, Aalborg, USA). Then an average produced gas flow rate was determined in every five minutes. A digital video camera was used to record the respective cumulative volumes of the produced oil and brine at different times.

The general procedure for preparing each CO₂ coreflood test is described below. First, the sandstone reservoir core plugs were placed in series inside the Dean–Stark extractor and thoroughly cleaned with toluene, methanol, and chloroform in sequence for 7–10 days to remove hydrocarbons, salts, and clays, respectively. After the sandstone reservoir core plugs were cleaned and dried, they were assembled in series in the horizontal coreholder and vacuumed for 24 h. Then, the cleaned reservoir brine was used as a working fluid and injected to measure the porosity of the composite core plugs.
Afterward, the cleaned reservoir brine was injected at different flow rates \( q_w = 0.1 - 0.5 \text{ cm}^3/\text{min} \) to measure the absolute permeability of the composite core plugs. Next, the original light oil was injected at \( q_{oil} = 0.1 \text{ cm}^3/\text{min} \) through the reservoir brine-saturated composite core plugs until no more brine was produced, i.e., the connate water saturation was achieved. The initial oil saturation process was purposely conducted at \( T_{lab} = 22.0 \text{ °C} \) to obtain a high initial oil saturation close to the actual high oil saturation in a tight sandstone formation. After the connate water saturation and initial oil saturation were reached at \( T_{lab} = 22.0 \text{ °C} \), the heating gun and the temperature controller were used to increase the temperature inside the airbath to \( T_{res} = 53.0 \text{ °C} \) and maintain this temperature for at least two days. Finally, a total of 3.0 PV of the original light oil was further injected to pressurize the composite core plugs to the specific production pressure, prior to each coreflood test.

A total of five coreflood (waterflooding + CO\(_2\) flooding) tests with five different extents of waterflooding were conducted in order to identify an optimum timing for the subsequent CO\(_2\)-EOR in a tight sandstone formation. They were roughly divided into three major cases: early, intermediate, and mature waterflooding, prior to CO\(_2\) flooding. In these five coreflood tests, waterflooding was terminated respectively when its secondary oil RF approximately reached 0, 25, 50, 75, and 100\% of its maximum value. The maximum secondary oil RF of 40\% in terms of the OOIP was estimated from Test #5, in which waterflooding was conducted until water BT happened at 0.19 PV. Therefore, Tests #1 and #2 were early waterflooding cases, Test #3 was an intermediate waterflooding case, Tests #4 and #5 were mature waterflooding cases. All the coreflood tests were conducted at \( T_{res} = 53.0 \text{ °C} \) and \( P_{prod} = 12.0 \text{ MPa} \), which was 1.0 MPa higher.
than the measured MMP of 11.0 MPa to ensure that the injected CO₂ could become miscible with the light crude oil through the so-called dynamic MCM process. Hence, they were miscible CO₂ secondary (Test #1) or tertiary (Tests #2–5) flooding processes. In Tests #2–5, a relatively low water injection rate of \( q_w = 0.1 \text{ cm}^3/\text{min} \) was purposely applied in the waterflooding process in order to achieve a high secondary oil RF. The CO₂ injection rate of \( q_{CO_2} = 0.4 \text{ cm}^3/\text{min} \) was used and each CO₂ flooding process was terminated after a total of 2.0 PV of CO₂ was injected.

A total of six coreflood tests were conducted to study CO₂-soaking effect on miscible CO₂ flooding in a tight sandstone formation. They can be roughly divided into the following four cases: CO₂ secondary flooding (i.e., no pre-waterflooding) without CO₂ soaking as a base case (Tests #6 and #7) for comparison purpose; CO₂ secondary flooding (i.e., no pre-waterflooding) with CO₂ soaking (Tests #8 and #9); pre-waterflooding plus CO₂ tertiary flooding without CO₂ soaking (Test #10) and with CO₂ soaking (Test #11). More specifically, in CO₂ secondary or tertiary flooding without CO₂ soaking, a total of 2.0 PV of CO₂ was injected continuously with no pre-waterflooding (Tests #6 and #7) or with pre-waterflooding (Test #10). In CO₂ secondary or tertiary flooding with CO₂ soaking, the first PV of CO₂ was injected continuously with no pre-waterflooding (Tests #8 and #9) or with pre-waterflooding (Test #11). Then, the reservoir core plugs together with the residual oil and reservoir brine were soaked with the injected CO₂ for 24 h. During each CO₂-soaking process, the inlet and outlet valves of the coreholder were closed and the inlet and outlet pressures of the coreholder were monitored and recorded by using the digital pressure indicator. Finally, the inlet and outlet valves were opened and the second PV of CO₂ was injected continuously to
recover the CO₂-soaked residual reservoir fluids. It should be noted that there was a short repressurization process after the soaking period and before the second PV of CO₂ was injected.

It is worthwhile to point out that there were three exceptions in this work. First, the CO₂ injection rates in five miscible CO₂ secondary or tertiary flooding processes were set to be \( q_{\text{CO₂}} = 0.4 \text{ cm}^3/\text{min} \). A lower CO₂ injection rate of \( q_{\text{CO₂}} = 0.2 \text{ cm}^3/\text{min} \) was chosen in Test #7 to study how a lower CO₂ injection rate (i.e., a longer CO₂ retention time) could affect the oil RF of continuous CO₂ secondary flooding. Second, five tests were conducted at the production pressure of \( P_{\text{prod}} = 12.0 \text{ MPa} \), whereas Test #9 was performed at a higher production pressure of \( P_{\text{prod}} = 16.0 \text{ MPa} \) to examine the effects of the production pressure on the CO₂-soaking process and on the second CO₂-flooding period. Third, a low water injection rate of \( q_w = 0.1 \text{ cm}^3/\text{min} \) in Tests #10 and #11 with pre-waterflooding was applied purposely until water broke through so as to achieve a high secondary oil RF of pre-waterflooding, prior to the subsequent continuous CO₂ tertiary flooding.
CHAPTER 4 RESULTS AND DISCUSSION

4.1 Mutual Interactions in the Light Oil/Reservoir Brine–CO₂ Systems

4.1.1 Saturation pressure and oil-swelling factor

The measured saturation pressures and oil SFs of four light oil–CO₂ systems at $T_{\text{res}} = 53.0 \, ^{\circ}\text{C}$ are listed in Table 4.1. In this study, the saturation pressure of each light oil–CO₂ system is determined from the sudden change point of the slope of its $P_{\text{cell}}$ versus $v_{\text{mix}}$ curve, which is plotted in Figure 4.1. The measured $P_{\text{cell}}$ is reduced with $v_{\text{mix}}$ in two distinct ranges. In Range I, $P_{\text{cell}}$ decreases drastically with a slight increase of $v_{\text{mix}}$. This is because at $P_{\text{cell}} \geq P_{\text{sat}}$, the light oil–CO₂ mixture is in a liquid phase, which is almost incompressible. In Range II, $P_{\text{cell}}$ decreases slightly with a substantial increase of $v_{\text{mix}}$. A large amount of dissolved CO₂ is released from the light oil–CO₂ mixture, which becomes highly compressible especially when $P_{\text{cell}}$ is slightly lower than $P_{\text{sat}}$. A linear equation is obtained by applying the linear regression of the measured $P_{\text{cell}}$–$v_{\text{mix}}$ data points in each range. Then the intersection point of the two linear equations is determined to be the saturation point, whose pressure is referred to as the saturation pressure, $P_{\text{sat}}$. It is found that $P_{\text{sat}}$ of CO₂-saturated light oil increases from 4.97 to 8.44 MPa as CO₂ concentration in the light oil–CO₂ mixture increases from 38.94 to 60.46 mol.% . It is noted that the $v_{\text{mix}}$ of CO₂-saturated light oil is reduced and then increased when the saturation pressure of the CO₂-saturated light oil increases. This may be because when the saturation pressure is relatively low, the pressure has a relatively stronger effect on the $v_{\text{mix}}$ of CO₂-saturated light oil. However, the CO₂ concentration plays a more important role in determining the $v_{\text{mix}}$ of CO₂-saturated light oil when the saturation pressure is relatively high.
Table 4.1  Measured saturation pressures ($P_{\text{sat}}$), gas–oil ratios (GORs), oil-swelling factors (SFs), and viscosities ($\mu_{\text{mix}}$) of four light oil–CO$_2$ systems with different CO$_2$ concentrations at $T_{\text{res}} = 53.0$ °C.

<table>
<thead>
<tr>
<th>Test no.</th>
<th>light oil–CO$_2$ system</th>
<th>$P_{\text{sat}}$ (MPa)</th>
<th>SF</th>
<th>GOR$^a$ (cm$^3$ CO$_2$/cm$^3$ oil)</th>
<th>GOR$^b$ (cm$^3$ CO$_2$/cm$^3$ oil)</th>
<th>$\mu_{\text{mix}}$ (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>61.06</td>
<td>38.94</td>
<td>4.97</td>
<td>1.14</td>
<td>56.9</td>
<td>59.0</td>
</tr>
<tr>
<td>2</td>
<td>52.87</td>
<td>47.13</td>
<td>6.25</td>
<td>1.19</td>
<td>79.5</td>
<td>88.9</td>
</tr>
<tr>
<td>3</td>
<td>45.02</td>
<td>54.98</td>
<td>7.60</td>
<td>1.26</td>
<td>108.9</td>
<td>108.4</td>
</tr>
<tr>
<td>4</td>
<td>39.54</td>
<td>60.46</td>
<td>8.44</td>
<td>1.34</td>
<td>136.4</td>
<td>149.5</td>
</tr>
</tbody>
</table>

$^a$Measured GOR at the standard conditions from Eq. (3.3)

$^b$Measured GOR at the standard conditions from Eq. (3.4)
Figure 4.1  $P_{\text{cell}}$–$v_{\text{mix}}$ diagrams of four light oil–CO$_2$ systems with different CO$_2$ concentrations at $T_{\text{res}} = 53.0$ °C.
The oil SF of CO₂-saturated light oil increases substantially from 1.14 to 1.34 in the same CO₂ concentration range. The oil-swelling effect has three obvious benefits to CO₂-EOR. First, a relatively large amount of oil can be produced from the reservoir as the oil volume increases. Second, the oil-swelling effect increases the residual oil saturation and thus the oil relative permeability, which results in a higher oil production rate. Third, the oil-swelling effect helps the residual oil trapped by water to swell and displace the water, which weakens the waterblocking effect [Grogan and Pinczewski, 1987]. The above-mentioned CO₂-EOR benefits become even stronger in the CO₂-soaking process, in which the residual reservoir fluids and the injected CO₂ strongly interact with each other in a much longer time.

### 4.1.2 GOR and GWR

Table 4.1 also summarizes the specific compositions of four light oil–CO₂ mixtures and their measured GORs at $T_{\text{res}} = 53.0$ °C. The first measured GOR was obtained from Eq. (3.3) with the measured volumes of the light oil and CO₂ inside the PVT cell, both of which became one phase at the saturation point. The second measured GOR was determined from Eq. (3.4) when the flashing method was applied by flashing a certain amount of CO₂-saturated light oil at the saturation point. It is found from Table 4.1 and Figure 4.2 that in general, the first measured GOR from the PVT tests was slightly lower than the second measured GOR from the flashing method, which was mainly attributed to two different experimental methods used in these two cases. The first method is based on the assumption that there is no immediate dissolution of CO₂ into the light oil at the very beginning of mixing, which may not be valid due to the strong mutual interaction between the light oil and CO₂. Thus the second measured GOR from the flashing
Figure 4.2  Measured gas–oil ratios (GORs) of the light oil–CO₂ system, measured gas–water ratios (GWRs) of the reservoir brine–CO₂ system, and predicted GWRs of pure water–CO₂ system at different saturation or equilibrium pressures and $T_{res} = 53.0 ^\circ C$. 


method is more accurate than the first measured GOR from the PVT tests. Table 4.2 lists and compares the measured GWRs of CO$_2$-saturated reservoir brine and the predicted GWRs of CO$_2$-saturated pure water at six different pressures and $T_{\text{res}} = 53.0$ °C. The first measured GWR (cm$^3$ CO$_2$/cm$^3$ brine) determined from Eq. (3.5) was for CO$_2$-saturated reservoir brine, whereas the second predicted GWR (cm$^3$ CO$_2$/cm$^3$ water) obtained from the CMG WinProp module was for CO$_2$-saturated pure water. It is found from Table 4.2 and Figure 4.2 that the second predicted GWR of CO$_2$-saturated pure water (i.e., carbonated water) is 25–50% higher than the first measured GWR of CO$_2$-saturated reservoir brine at the same test conditions. The TDS or salinity of the reservoir brine was equal to 4,230 mg/L at 180 °C, which led to a much lower GWR of CO$_2$-saturated reservoir brine, in comparison with that of CO$_2$-saturated pure water. Figure 4.2 shows and compares the measured GORs and determined GWRs at different equilibrium pressures and $T_{\text{res}} = 53.0$ °C. In general, the measured GOR was about six times of the measured GWR at the same equilibrium pressure and temperature. Much more CO$_2$ dissolved into the light oil than that into the reservoir brine under the same reservoir conditions. On the other hand, the measured GWRs of the reservoir brine–CO$_2$ system at different equilibrium pressures and $T_{\text{res}} = 53.0$ °C also show that dissolution of CO$_2$ into the saline brine still holds a tremendous potential for CO$_2$ storage in the depleted oil/gas reservoirs or deep saline aquifers.

Dissolution of CO$_2$ into the reservoir oil and brine tends to mobilize and recover the trapped residual oil after the primary and/or secondary recovery. In order to interact with the trapped residual oil in a tight oil formation, CO$_2$ has to dissolve first into the reservoir brine and then into the trapped oil through the CO$_2$-saturated reservoir brine
Table 4.2  Measured and predicted gas–water ratios (GWRs) at six different equilibrium pressures and $T_{\text{res}} = 53.0$ °C.

<table>
<thead>
<tr>
<th>Test no.</th>
<th>$P_{\text{eq}}$ (MPa)</th>
<th>GWR$^a$ (cm$^3$ CO$_2$/cm$^3$ brine)</th>
<th>GWR$^b$ (cm$^3$ CO$_2$/cm$^3$ water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.15</td>
<td>13.0</td>
<td>19.5</td>
</tr>
<tr>
<td>2</td>
<td>7.01</td>
<td>14.2</td>
<td>21.2</td>
</tr>
<tr>
<td>3</td>
<td>8.09</td>
<td>15.6</td>
<td>22.9</td>
</tr>
<tr>
<td>4</td>
<td>8.51</td>
<td>16.2</td>
<td>23.5</td>
</tr>
<tr>
<td>5</td>
<td>9.58</td>
<td>18.3</td>
<td>24.8</td>
</tr>
<tr>
<td>6</td>
<td>10.85</td>
<td>20.7</td>
<td>25.9</td>
</tr>
</tbody>
</table>

$^a$Measured GWR of the reservoir brine–CO$_2$ system at the standard conditions from Eq. (3.5)

$^b$Predicted GWR of the pure water–CO$_2$ system at the standard conditions from the CMG WinProp module
After a certain amount of CO₂ dissolves into the trapped oil, it swells, becomes diluted, and may be recovered in CO₂-EOR process [Campbell and Orr, 1985]. Moreover, the IFT between the reservoir oil and brine is also reduced with the dissolution of CO₂ into the two phases, which helps to displace the trapped oil [Yang et al., 2005]. Due to slow dissolution and limited solubility of CO₂ into the reservoir brine, nevertheless, dissolution of CO₂ into the trapped oil through the CO₂-saturated reservoir brine is slow and limited. Hence, recovery of the trapped residual oil through CO₂ molecular diffusion alone takes a long time.

### 4.1.3 Viscosity of CO₂-saturated light oil

In this study, the viscosity of each CO₂-saturated light oil is determined from Eq. (3.6) and also tabulated in Table 4.1. The measured viscosity of each light oil–CO₂ system is reduced as the CO₂ concentration in the light oil is increased. The CO₂-saturated light oil viscosities at the respective CO₂ concentrations of 38.94 and 60.46 mol.% and \( T_{\text{res}} = 53.0 \, ^{\circ}\text{C} \) are lower than 16% and 10% of the dead light oil viscosity of \( \mu_{\text{oil}} = 6.27 \, \text{mPa} \cdot \text{s} \) at the same reservoir temperature. The reduced oil viscosity contributes to the oil recovery in the continuous CO₂ flooding. When CO₂ concentration in the residual light oil increases, the CO₂-saturated residual oil with a lower viscosity becomes much more mobile or has a higher mobility. In addition, the mobility ratio of the displacing phase (i.e., the injected CO₂) to the displaced phase (i.e., the CO₂-saturated residual oil) is considerably reduced, which results in a higher CO₂ sweeping efficiency.
4.1.4 IFT between the light oil/reservoir brine and CO₂

Figure 4.3 shows and compares the measured equilibrium IFTs between the light oil and CO₂ and those between the reservoir brine and CO₂ at different equilibrium pressures and \( T_{\text{res}} = 53.0 ^\circ \text{C} \). As expected, the measured equilibrium IFT between the light oil/reservoir brine and CO₂ is reduced as the equilibrium pressure is increased. This is due to an increased solubility of CO₂ in the light oil/reservoir brine at an increased equilibrium pressure. It is seen from Figure 4.3 that under the same test conditions, the measured equilibrium IFT between the reservoir brine and CO₂ is approximately three to ten times of that between the light oil and CO₂.

In general, a higher IFT leads to a higher capillary pressure. Thus, the capillary pressure between the reservoir brine and CO₂ is substantially higher than that between the light oil and CO₂ under the coreflood test conditions used in this study, i.e., \( P_{\text{res}} = 12.0 \text{ MPa} \) and \( T_{\text{res}} = 53.0 ^\circ \text{C} \). In addition, the IFT between two phases in contact also affects their relative motion or displacement. The capillary number is an important dimensionless number, which is often used to evaluate the displacement efficiency and defined as the ratio of the viscous force to the capillary force:

\[
N_{ca} = \frac{\nu \mu}{\phi \gamma_{eq}}
\]  

(4.1)

where, \( \nu \) and \( \mu \) are the linear velocity and viscosity of the injected fluid (brine or CO₂) under the reservoir conditions; \( \phi \) is the reservoir porosity and \( \gamma_{eq} \) is the equilibrium IFT between the displaced fluid (oil or brine) and displacing fluid (brine or CO₂). Since the IFT of the reservoir brine–CO₂ system is about three to ten times of that of the light
Figure 4.3  Measured equilibrium interfacial tensions (IFTs) between the light oil or reservoir brine and CO₂ at different equilibrium pressures and $T_{\text{res}} = 53.0$ °C.
oil–CO$_2$ system, the capillary number of the former system is about one third to one tenth of that of the latter system. A small capillary number results in a poor displacement efficiency. Therefore, in the miscible CO$_2$ tertiary flooding process, the displacement efficiency for the injected CO$_2$ to displace the reservoir brine is low. This fact indicates that the subsequently injected CO$_2$ tends to bypass the initially injected reservoir brine in the waterflooded area, which adversely affects the recovery of the residual oil trapped by the reservoir brine. On the other hand, the capillary number of the light oil–CO$_2$ system in the area unswept by water is much larger. Hence, the injected CO$_2$ is more likely to sweep and displace the residual oil in this area. The sweeping efficiency is increased as more area is touched and swept by CO$_2$. Also a high displacement efficiency can be achieved in the miscible CO$_2$ flooding process.

4.1.5 MMP and $P_{\text{max}}$ of light oil–CO$_2$ system

In this study, the measured equilibrium IFTs between the light oil and CO$_2$ at different equilibrium pressures of $P_{\text{eq}} = 1.0$–12.4 MPa and a constant temperature of $T_{\text{res}} = 53.0$ °C are further replotted in Figure 4.4. It is found from this figure that the measured equilibrium IFT is reduced almost linearly with the equilibrium pressure in two distinct pressure ranges: Range I ($P_{\text{eq}} = 1.0$–8.5 MPa) and Range II ($P_{\text{eq}} = 8.5$–12.4 MPa). Based on the measured data (symbols) in Figure 4.4, the equilibrium IFT $\gamma_{\text{eq}}$ (mJ/m$^2$) between the light oil and CO$_2$ is correlated to the equilibrium pressure $P_{\text{eq}}$ (MPa) by applying the liner regression in the above-mentioned two equilibrium pressure ranges, respectively:
Figure 4.4  Measured equilibrium interfacial tensions (IFTs) between the light oil and CO$_2$ at different equilibrium pressures and $T_{res} = 53.0$ °C.

Range I: $\gamma_{eq} = -1.973 P_{eq} + 21.759$
\[(1.0 \text{ MPa} \leq P_{eq} \leq 8.5 \text{ MPa}, R^2 = 0.989)\]

Range II: $\gamma_{eq} = -0.414 P_{eq} + 8.556$
\[(8.5 \text{ MPa} \leq P_{eq} \leq 12.4 \text{ MPa}, R^2 = 0.993)\]
\[ \gamma_{eq} = -1.973 P_{eq} + 21.759 \quad (1.0 \text{ MPa} \leq P_{eq} \leq 8.5 \text{ MPa}, R^2 = 0.989), \quad (4.2) \]

\[ \gamma_{eq} = -0.414 P_{eq} + 8.556 \quad (8.5 \text{ MPa} \leq P_{eq} \leq 12.4 \text{ MPa}, R^2 = 0.993). \quad (4.3) \]

According to the VIT technique, which is based on the concept that the equilibrium IFT between the oil and gas phases approaches zero when these two phases become miscible, the MCM pressure or the MMP is defined as the pressure at the intersection point between Eq. (4.2) and the abscissa. Thus the MMP is determined to be 11.0 MPa for the light oil–CO₂ system tested in this study. Furthermore, the first-contact miscibility (FCM) pressure \( P_{\text{max}} \) is determined as the pressure at the intersection point between Eq. (4.3) and the abscissa, which is found to be 20.7 MPa.
4.2 Optimum Timing for Miscible CO₂-EOR after Waterflooding

4.2.1 Gas production and CO₂ BT

The measured average produced gas flow rates in Test #1–5 are plotted in Figure 4.5 (a–e). No gas was produced in the waterflooding process or at the beginning of each CO₂ flooding process. As more CO₂ was injected, gas started to produce from the core plugs. The early produced gas was predominantly the dissolved CO₂, which was co-produced with and flashed from the produced oil. There was no free-gas production or CO₂ BT at this stage. Then the gas flow rate increased quickly, reached a “peak” value, and remained relatively high. The PV of the injected CO₂ at which the gas flow rate reached the “peak” value was defined as the PV of CO₂ BT in this study. Two different PVs of CO₂ BT were found and are listed in Table 4.3: one from the beginning of waterflooding and the other from the beginning of CO₂ flooding alone. After CO₂ BT, the subsequently injected CO₂ simply followed the CO₂-BT channels and was produced rapidly, which was indicated by the relatively high gas flow rates.

The PVs of CO₂ BTs from the beginning of CO₂ flooding for Tests #1–5 tabulated in Table 4.3 are further plotted in Figure 4.6. CO₂ BT is delayed as long as there is waterflooding. More specifically, CO₂ BT occurred at 0.40 PV in Test #1 without waterflooding. This early CO₂ BT was attributed to an extremely low viscosity of CO₂ under the test conditions. Based on the prediction from the CMG WinProp module, \( \mu_{\text{CO}_2} \) is equal to 0.04 mPa·s at \( P_{\text{res}} = 12.0 \text{ MPa} \) and \( T_{\text{res}} = 53.0 \text{ °C} \), which is much lower than that of the light oil or the reservoir brine under the same reservoir conditions. Thus severe CO₂ viscous fingering through the core plugs occurred and led to an early CO₂
Table 4.3  Physical properties and oil recovery factors of five coreflood tests with different starting timings of CO₂ tertiary flooding after waterflooding at the production pressure of $P_{\text{prod}} = 12.0 \text{ MPa}$ and reservoir temperature of $T_{\text{res}} = 53.0 \text{ °C}$.

<table>
<thead>
<tr>
<th>Test no.</th>
<th>$k$ (mD)</th>
<th>$\phi$ (%)</th>
<th>$S_{\text{oi}}$ (%)</th>
<th>$S_{\text{wc}}$ (%)</th>
<th>Water RF (%)</th>
<th>CO₂ RF&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Total RF (%)</th>
<th>CO₂ RF&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>WF (PV)</th>
<th>CO₂ BT&lt;sup&gt;a&lt;/sup&gt; (PV)</th>
<th>CO₂ BT&lt;sup&gt;b&lt;/sup&gt; (PV)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.71</td>
<td>12.68</td>
<td>62.67</td>
<td>37.33</td>
<td>0.00</td>
<td>63.22</td>
<td>63.22</td>
<td>63.22</td>
<td>0.00</td>
<td>0.40</td>
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</tr>
<tr>
<td>2</td>
<td>2.91</td>
<td>12.96</td>
<td>62.73</td>
<td>37.27</td>
<td>9.88</td>
<td>67.49</td>
<td>77.37</td>
<td>74.89</td>
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<td>1.00</td>
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</tr>
<tr>
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<td>0.40</td>
<td>12.55</td>
<td>69.02</td>
<td>30.98</td>
<td>20.49</td>
<td>62.55</td>
<td>83.04</td>
<td>78.67</td>
<td>0.15</td>
<td>1.40</td>
<td>1.25</td>
</tr>
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<td>13.79</td>
<td>56.42</td>
<td>43.58</td>
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<td>50.00</td>
<td>80.04</td>
<td>71.47</td>
<td>0.17</td>
<td>0.80</td>
<td>0.63</td>
</tr>
<tr>
<td>5</td>
<td>0.28</td>
<td>12.74</td>
<td>55.83</td>
<td>44.17</td>
<td>37.09</td>
<td>41.31</td>
<td>78.40</td>
<td>65.67</td>
<td>0.19</td>
<td>0.90</td>
<td>0.71</td>
</tr>
</tbody>
</table>

$k$: absolute permeability  
$\phi$: porosity  
$S_{\text{oi}}$: initial oil saturation  
$S_{\text{wc}}$: connate water saturation  
Water RF: oil recovery factor (RF) of waterflooding in terms of the original-oil-in-place (OOIP)  
CO₂ RF<sup>a</sup>: oil RF of CO₂ flooding in terms of the OOIP  
Total RF: total oil RF of waterflooding and CO₂ flooding in terms of the OOIP  
CO₂ RF<sup>b</sup>: oil RF of CO₂ flooding in terms of the residual-oil-in-place (ROIP)  
WF: at which (PV) waterflooding was terminated  
CO₂ BT<sup>a</sup>: at which (total PV) CO₂ breakthrough (BT) occurred from the beginning of waterflooding. This CO₂ BT for each test is marked in Figures 4.5 (a–e)  
CO₂ BT<sup>b</sup>: at which (PV) CO₂ BT occurred from the beginning of CO₂ flooding. This CO₂ BT for each test is mentioned in the context and plotted in Figure 4.6
Figure 4.5  (a) Measured oil RF in terms of the OOIP, average gas flow rate ($q_g$), and cumulative water production ($Q_w$) in Test #1 (0% waterflooding + CO$_2$ flooding) at $P_{\text{prod}} = 12.0$ MPa and $T_{\text{res}} = 53.0$ °C.
Figure 4.5  (b) Measured oil RF in terms of the OOIP, average gas flow rate ($q_g$), and cumulative water production ($Q_w$) in Test #2 (25% waterflooding + CO$_2$ flooding) at $P_{prod} = 12.0$ MPa and $T_{res} = 53.0$ °C.
Figure 4.5 (c) Measured oil RF in terms of the OOIP, average gas flow rate ($q_g$), and cumulative water production ($Q_w$) in Test #3 (50% waterflooding + CO$_2$ flooding) at $P_{prod}$ = 12.0 MPa and $T_{res}$ = 53.0 °C.
Figure 4.5  (d) Measured oil RF in terms of the OOIP, average gas flow rate \((q_g)\), and cumulative water production \((Q_w)\) in Test #4 (75% waterflooding + CO\(_2\) flooding) at \(P_{\text{prod}} = 12.0\) MPa and \(T_{\text{res}} = 53.0\) °C.
Figure 4.5  (e) Measured oil RF in terms of the OOIP, average gas flow rate ($q_g$), and cumulative water production ($Q_w$) in Test #5 (100% waterflooding + CO$_2$ flooding) at $P_{\text{prod}} = 12.0$ MPa and $T_{\text{res}} = 53.0$ °C.
Figure 4.6  Measured total oil RFs of waterflooding and CO$_2$ flooding in terms of the OOIP, oil RFs of CO$_2$ flooding in terms of the ROIP, and PVs of CO$_2$ BT from the beginning of CO$_2$ flooding for Tests #1–5 with five different secondary oil RFs of 0, 9.88, 20.49, 30.04, and 37.09%, which were approximately equivalent to five different waterflooding extents of 0, 25, 50, 75, and 100%, prior to CO$_2$ flooding.
BT in this test. In Test #2, waterflooding was terminated when its secondary oil RF reached 9.88%, which was approximately equivalent to 25% of the estimated maximum secondary oil RF of 40% in terms of the OOIP. The PV of CO₂ BT was significantly increased to 0.94 PV. This large delay of CO₂ BT was due to a much smaller mobility contrast between the initially injected reservoir brine and the subsequently injected CO₂ in CO₂ tertiary flooding than that between the residual light oil and the injected CO₂ in CO₂ secondary flooding. Thus CO₂ viscous fingering was considerably suppressed in Test #2. The CO₂ BT was further delayed to 1.25 PV in Test #3, in which waterflooding was stopped at 50% when its secondary oil RF reached 20.49% and CO₂ flooding was commenced afterward. It is also found that the gas flow rates after CO₂ BT in Tests #2 and #3 were more stable and lower than that in Test #1, which indicated a better mobility control of CO₂ in these two tests.

However, delay of CO₂ BT in a test with a large amount of the injected water was not as much as that in a test with a small to moderate amount of the injected water. CO₂ BT occurred at 0.63 PV in Test #4 with 75% waterflooding or the secondary oil RF of 30.04%, whereas it took place at 0.71 PV in Test #5 with 100% waterflooding or the secondary oil RF of 37.09%. These two PVs of CO₂ BT were significantly smaller than those in Tests #2 and #3 but still considerably larger than that in Test #1. Moreover, the gas flow rates in these two tests had a similar trend as that in Test #1, which was increased quickly to a peak value and then decreased gradually after CO₂ BT. With a large extent of waterflooding, water displacement front was close to the production well and some water channels were formed inside the core plugs with higher permeabilities. Hence, the subsequently injected CO₂ tended to preferentially follow the established
water channels and quickly broke through the core plugs. The measured cumulative water production data and the average gas flow rates plotted in Figures 4.5 (d and e) for Tests #4 and #5 clearly show that water was produced soon after CO₂ was injected. In particular, water production started immediately after CO₂ was injected in Test #5. Furthermore, CO₂ BT occurred not too long after water production in either test. The above-mentioned water and gas production trends indicate that if waterflooding is conducted to a large extent, CO₂ tends to preferentially follow the existing water channels, displace the initially injected water rather than the trapped residual oil, and quickly break through the core plugs.

In addition, the PV of CO₂ BT also strongly affects the mutual interactions between the reservoir fluids and the injected CO₂. It is well known that such interactions take a long time in a tight formation. Before CO₂ BT, CO₂ can diffuse laterally into a large unswept area in a long interaction time. Hence, more oil can be touched and swept by CO₂ until it is produced by CO₂. After CO₂ BT occurs, nevertheless, CO₂ tends to flow through the existing water channels only and thus its interactions with the reservoir fluids are inadequate to recover the trapped residual oil. It is concluded that a larger PV of CO₂ BT represents longer and stronger interactions between the reservoir fluids and the injected CO₂ so that more trapped residual oil is touched, swept, and ultimately recovered before CO₂ BT.

4.2.2 Oil recovery process and factor

Table 4.3 lists the oil RFs of waterflooding in terms of the OOIP, the oil RFs of CO₂ flooding in terms of the OOIP, the total oil RFs of waterflooding and CO₂ flooding in terms of the OOIP, and the oil RFs of CO₂ flooding in terms of the ROIP for Tests #1–5.
Figures 4.5 (a–e) show the measured oil RF in terms of the OOIP versus the injected PV of water and/or CO₂ in each test. As expected, the oil RF was increased with the injected PV of water or CO₂. The oil RF was increased almost linearly with the injected PV of water in the waterflooding process. This trend was attributed to an extremely low compressibility of the injected reservoir brine. The waterflooding process was almost a volumetric displacement. On the other hand, as shown in Figures 4.5 (b–e) for Tests #2–5, a large incremental or enhanced oil RF was always achieved in each miscible CO₂ tertiary flooding process, which indicates great potential of CO₂-EOR after waterflooding. Unlike the secondary oil RF in the waterflooding process, the tertiary oil RF of each CO₂ flooding process was increased non-linearly with the injected PV of CO₂. Based on the measured oil RFs and average gas flow rates, the oil recovery process during CO₂ flooding can be approximately divided into the following three stages. In the initial oil recovery stage, the oil RF of CO₂ flooding was increased slowly and no gas was produced as the injected CO₂ dissolved into the reservoir fluids at the beginning of CO₂ flooding. In the second oil recovery stage, CO₂-diluted oil was produced quickly with moderate gas production. Most oil was produced in such a quick production stage. At the end of this stage, CO₂-diluted oil reached the outlet of the coreholder or the production well in the reservoir and CO₂ BT almost occurred. After CO₂ BT occurred, only a limited amount of oil was slowly produced in the final oil production stage. This slow oil production was due to an extremely low oil relative permeability and the produced light oil was primarily composed of the light to intermediate hydrocarbons extracted by supercritical CO₂ after CO₂ BT. The light oil produced in this stage had a much lighter colour from the laboratory observations.
Figure 4.6 summarizes the total oil RFs of waterflooding and CO₂ flooding in terms of the OOIP, the oil RFs of CO₂ flooding in terms of the ROIP, the PVs of CO₂ BT from the beginning of CO₂ flooding in Tests #1–5. In this study, the total oil RF of waterflooding and CO₂ flooding in terms of the OOIP is defined as the ratio of the total produced oil in the waterflooding and CO₂ flooding processes to the OOIP to evaluate the overall performance of waterflooding and CO₂ flooding. The oil RF of CO₂ flooding in terms of the ROIP is defined as the ratio of the produced oil in the miscible CO₂ tertiary flooding process to the ROIP after the waterflooding process to evaluate the specific performance of CO₂ tertiary flooding alone. It is found from Table 4.3 and Figure 4.6 that the total oil RFs of waterflooding and CO₂ flooding in terms of the OOIP in the tests with the initial waterflooding and subsequent CO₂ flooding are much higher than that in Test #1. Waterflooding has the lowest oil RF in comparison with CO₂ flooding. It is also found from Table 4.3 and Figure 4.6 that the oil RFs of CO₂ flooding in terms of the ROIP in the tests with the waterflooding process are much higher than that in Test #1, in which only miscible CO₂ secondary flooding process was conducted. These facts show that the initially injected water helps the subsequently injected CO₂ to perform better due to a better CO₂ mobility control, which is attributed to a reduced CO₂ relative permeability at a reduced CO₂ saturation. In summary, the total oil RFs of waterflooding and CO₂ flooding in terms of the OOIP, the oil RFs of CO₂ flooding in terms of the ROIP, and the PVs of CO₂ BT from the beginning of CO₂ flooding all reached their maximum values if waterflooding was terminated at 50% (Test #3). It was a better CO₂ mobility control and a weaker waterblocking effect in this test that jointly resulted in the optimum miscible CO₂ tertiary flooding after 50% or intermediate waterflooding.
4.3 Soaking Effect on Miscible CO$_2$ Flooding

4.3.1 Pressure decay in CO$_2$-soaking process

In this study, CO$_2$-soaking process was conducted after 1.0 PV of CO$_2$ injection, in which CO$_2$ BT had already occurred. Hence, there was a good connectivity between the injector and producer through CO$_2$-BT channels. The pressure difference between the inlet and outlet was relatively small. The reduction of their average value with time inside the coreholder in each test was used to characterize the pressure decay in CO$_2$-soaking process. The measured average pressures between the inlet and outlet of the coreholder during CO$_2$-soaking processes in Tests #8, #9, and #11 are plotted in Figure 4.7. The initial pressure ($P_{ini}$) at the beginning and the equilibrium pressure ($P_{eq}$) at the end of each CO$_2$-soaking process are given in Table 4.4.

It is seen from Figure 4.7 that in all three tests with CO$_2$ soaking, the measured average pressure inside the reservoir core plugs was quickly reduced at the beginning and reached a stable value at the end of each CO$_2$-soaking process, while CO$_2$ was dissolved into the residual reservoir fluids. In Test #8, the pressure decay between the initial pressure ($P_{ini} = 12.1$ MPa) and equilibrium pressure ($P_{eq} = 7.0$ MPa) in CO$_2$ soaking was equal to 5.1 MPa. This large pressure decay was attributed to a high solubility of CO$_2$ in the light oil. In Test #9 with a higher production pressure of $P_{prod} = 16.0$ MPa, the initial pressure ($P_{ini} = 16.2$ MPa) was 4.1 MPa higher than that in Test #8 and the equilibrium pressure ($P_{eq} = 8.6$ MPa) at the end of CO$_2$ soaking was only 1.6 MPa higher than that in Test #8, respectively. Obviously, a higher equilibrium pressure led to higher solubilities of CO$_2$ in both the residual oil and the reservoir brine. Therefore, the oil-swelling effect,
Table 4.4   Physical properties and oil recovery factors of six coreflood tests with different flooding processes in tight sandstone core plugs at different test conditions and $T_{\text{res}} = 53.0 \, ^\circ \text{C}$.

<table>
<thead>
<tr>
<th>test no.</th>
<th>$k$ (mD)</th>
<th>$\phi$ (%)</th>
<th>$S_{\text{oi}}$ (%)</th>
<th>Water RF (%)</th>
<th>$q_{\text{CO}_2}$ (cm$^3$/min)</th>
<th>$P_{\text{prod}}$ (MPa)</th>
<th>CO$_2$ RF$^a$ (%)</th>
<th>$P_{\text{ini}}$ (MPa)</th>
<th>$P_{eq}$ (MPa)</th>
<th>CO$_2$ RF$^b$ (%)</th>
<th>Total RF (%)</th>
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<td>12</td>
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<td>–</td>
<td>–</td>
<td>0.77</td>
<td>63.22</td>
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<td>12</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>8</td>
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<td>62.43</td>
<td>0.00</td>
<td>0.4</td>
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<td>7.0</td>
<td>12.83</td>
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<td>13.01</td>
<td>56.07</td>
<td>0.00</td>
<td>0.4</td>
<td>16</td>
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<td>16.2</td>
<td>8.6</td>
<td>14.74</td>
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<td>20.35</td>
<td>12.7</td>
<td>8.5</td>
<td>11.05</td>
<td>80.43</td>
</tr>
</tbody>
</table>

Notes:

$k$: absolute permeability of the composite sandstone reservoir core plugs

$\phi$: porosity of the composite sandstone reservoir core plugs

$S_{\text{oi}}$: initial oil saturation

Water RF: oil RF of pre-waterflooding at $q_w = 0.1 \, \text{cm}^3/\text{min}$

$q_{\text{CO}_2}$: CO$_2$ injection rate in continuous CO$_2$-flooding period

$P_{\text{prod}}$: production pressure in CO$_2$-flooding period

CO$_2$ RF$^a$: oil RF of CO$_2$ flooding in the first PV of CO$_2$ injection

$P_{\text{ini}}$: initial average pressure at the beginning of CO$_2$ soaking

$P_{eq}$: equilibrium average pressure after CO$_2$ soaking for 24 h

CO$_2$ RF$^b$: oil RF of CO$_2$ flooding in the second PV of CO$_2$ injection

Total RF: total oil RF of pre-waterflooding and CO$_2$ flooding
Figure 4.7  Measured average pressures between the inlet and outlet of the composite reservoir core plugs versus soaking time ($t_{\text{soaking}}$) in Tests #8 and #9 (CO$_2$ secondary flooding with CO$_2$ soaking) and Test #11 (pre-waterflooding plus CO$_2$ tertiary flooding with CO$_2$ soaking).
oil viscosity reduction, IFT reduction, and other beneficial effects on CO\textsubscript{2}-EOR were more pronounced in Test #9. The pressure decay from the initial pressure ($P_{\text{ini}} = 12.7$ MPa) to the equilibrium pressure ($P_{\text{eq}} = 8.5$ MPa) of CO\textsubscript{2}-soaking process in Test #11 was the smallest (4.2 MPa) due to the highest water saturation after pre-waterflooding. From the PVT studies, the gas–water ratio (GWR) of CO\textsubscript{2}-saturated reservoir brine was measured to be approximately one-sixth of the GOR of CO\textsubscript{2}-saturated light oil at the same test pressure and reservoir temperature of $T_{\text{res}} = 53.0$ °C. Hence, CO\textsubscript{2} is much less soluble in the reservoir brine than in the light crude oil. This is why the equilibrium pressure at the end of CO\textsubscript{2} soaking in Test #11 was 1.5 MPa higher than that in Test #8.

In addition, Figure 4.7 also clearly shows that dissolution of CO\textsubscript{2} into the residual oil and reservoir brine in a tight formation is a slow mass-transfer process. It took 24 h for the injected CO\textsubscript{2} and the reservoir fluids to almost reach an equilibrium state inside the coreholder. This implies that a large amount of the crude oil was not saturated with CO\textsubscript{2} in a relatively quick displacement process, such as the continuous CO\textsubscript{2}-flooding process (3.5 h in Test #6) in a tight sandstone formation. The beneficial CO\textsubscript{2}-EOR mechanisms, such as the oil-swelling effect, IFT reduction, and oil viscosity reduction, could not reach their full potentials in such a short continuous CO\textsubscript{2}-flooding period. On the other hand, not only the injected CO\textsubscript{2} was further dissolved into the residual oil and reservoir brine in CO\textsubscript{2}-soaking process but it also became more HCs-enriched due to two-way mass transfer between the crude oil and injected CO\textsubscript{2}. In the second PV of CO\textsubscript{2} injection, the HCs-enriched CO\textsubscript{2} was produced along the crude oil and then some CO\textsubscript{2}-extracted HCs might condense and become part of the produced light crude oil again at the ambient conditions.
4.3.2 CO₂-soaking effect

Figure 4.8 shows the measured oil RFs and average produced gas flow rates versus the injected PVs of CO₂ in Tests #6 and #7, both of which were continuous CO₂ secondary flooding without CO₂ soaking. These two tests were conducted at the same production pressure of $P_{\text{prod}} = 12.0$ MPa but with two different constant CO₂ injection rates: $q_{\text{CO₂}} = 0.4$ cm$^3$/min in Test #6 and 0.2 cm$^3$/min in Test #7. The cumulative water production curves were not plotted in Figure 4.8 because there was no or little water production in the CO₂ secondary flooding tests. It is seen from this figure that the oil RF in Test #6 or #7 increased quickly at the beginning but slowly from CO₂ BT to the end. The CO₂ BT was considered to occur when there was a peak produced gas flow rate. An early CO₂ BT was attributed to an unfavourable mobility contrast between the injected CO₂ and light oil under reservoir conditions. The oil production post CO₂ BT was mainly due to CO₂-induced light-HCs extraction and oil-swelling effect. The final oil RF at 2.0 PV of CO₂ injection in Test #7 with a lower CO₂ injection rate was 5.48% higher than that in Test #6 with a higher CO₂ injection rate. Overall, reducing CO₂ injection rate increases the mutual interactions and retention time between the reservoir fluids and injected CO₂ so that a higher oil RF is obtained. Hence, it is expected that a much higher oil RF can be achieved if a CO₂-soaking process is implemented as an extreme case in the middle of the continuous CO₂ flooding. In this way, there are much stronger mutual interactions between the reservoir fluids and injected CO₂ over a much longer retention time.
Figure 4.8  Measured oil RFs and average produced gas flow rates of two CO\textsubscript{2} secondary flooding processes without CO\textsubscript{2} soaking at \( P_{\text{prod}} = 12.0 \, \text{MPa} \) in Test #6 (\( q_{\text{CO}_2} = 0.4 \, \text{cm}^3/\text{min} \)) and Test #7 (\( q_{\text{CO}_2} = 0.2 \, \text{cm}^3/\text{min} \)).
Figure 4.9 compares the measured oil RFs and average produced gas flow rates versus the injected PVs of CO₂ in Tests #6 and #8. Test #6 was CO₂ secondary flooding without CO₂ soaking, whereas Test #8 was CO₂ secondary flooding with CO₂ soaking for 24 h between the first and second injected PVs of CO₂. As expected, a large amount of the crude oil was produced and early CO₂ BT happened in the first PV of continuous CO₂ secondary flooding in these two tests. In the second PV of CO₂ injection, the oil RF increased marginally in Test #6 but considerably in Test #8 till the end. The final oil RF at 2.0 PV of CO₂ injection in Test #8 with CO₂ soaking for 24 h was 7.72% higher than that in Test #6 without CO₂ soaking. Obviously, CO₂ soaking considerably increases the final oil RF of CO₂ secondary flooding.

Figure 4.10 depicts the measured oil RFs and average produced gas flow rates versus the injected PVs of CO₂ in Tests #8 and #9, both of which were CO₂ secondary flooding with CO₂ soaking for 24 h between the first and second injected PVs of CO₂. However, they were conducted at two different production pressures: \( P_{\text{prod}} = 12.0 \text{ MPa} \) in Test #8 and 16.0 MPa in Test #9. It is seen from this figure that these two tests achieved similar oil RFs in the first PV of continuous CO₂ flooding. Thus increasing the production pressure does not appreciably increase the oil recovery as long as CO₂ secondary flooding is conducted under the miscible condition [Cao and Gu, 2013a]. The oil RFs in Tests #8 and #9 increased steadily in the second PV of continuous CO₂ flooding after CO₂ soaking, which were equal to 12.83% and 14.74%, respectively. The total oil RF in Test #9 was 3.25% higher than that in Test #8. This moderate increase was resulted from stronger mutual interactions between the reservoir fluids and injected
Figure 4.9  Measured oil RFs and average produced gas flow rates of two CO$_2$ secondary flooding processes at $P_{\text{prod}} = 12.0$ MPa in Test #6 without CO$_2$ soaking and Test #8 with CO$_2$ soaking.
Figure 4.10  Measured oil RFs and average produced gas flow rates of two CO₂ secondary flooding processes with CO₂ soaking in Test #8 ($P_{\text{prod}} = 12.0$ MPa) and Test #9 ($P_{\text{prod}} = 16.0$ MPa).
CO₂ in the CO₂-soaking process at a higher equilibrium pressure and in the continuous CO₂ secondary flooding process at a higher production pressure.

The measured oil RFs, cumulative water production data and average produced gas flow rates in Tests #10 and #11 were plotted and compared in Figures 4.11 (a and b), respectively. Both tests consisted of pre-waterflooding plus CO₂ tertiary flooding. Test #11 had CO₂ soaking for 24 h between the first and second injected PVs of CO₂, whereas Test #10 had no CO₂ soaking. The pre-waterflooding was conducted until water broke through in each test. During pre-waterflooding, the oil RF increased linearly with the injected PV of water as the injected water was incompressible so that the pre-waterflooding was a volumetric displacement process. At the beginning of the first PV of CO₂ injection, the oil RF increased marginally, while the water production increased quickly. Once CO₂-diluted light crude oil reached the outlet of the coreholder or the producer, the oil RF and produced gas flow rate started to increase suddenly. The gas production reached a peak value when CO₂ BT occurred and continued to be high afterwards. In comparison with the early CO₂ BTs of less than 0.5 PV in CO₂ secondary flooding of Tests #6–9 shown in Figures 4.8–4.10, CO₂ BT was significantly delayed in CO₂ tertiary flooding of Test #10 or #11, as shown in Figure 4.11 (b). The previously injected water effectively controlled the mobility of the subsequently injected CO₂ and led to a longer interaction time between the reservoir fluids and CO₂ before CO₂ BT. It is also seen from Figure 4.11 (b) that the cumulative water production in the second PV of continuous CO₂ tertiary flooding increased slowly in Test #10 without CO₂ soaking due to severe CO₂ channeling and weak mutual interactions between reservoir brine and CO₂. However, the cumulative water production in the second PV of continuous CO₂
Figure 4.11  (a) Measured oil RFs in Test #10 (pre-waterflooding plus CO$_2$ tertiary flooding without CO$_2$ soaking) and Test #11 (pre-waterflooding plus CO$_2$ tertiary flooding with CO$_2$ soaking).
Figure 4.11  (b) Measured cumulative water production and average produced gas flow rates in Test #10 (pre-waterflooding plus CO₂ tertiary flooding without CO₂ soaking) and Test #11 (pre-waterflooding plus CO₂ tertiary flooding with CO₂ soaking).
tertiary flooding increased steadily in Test #11 with CO₂ soaking. This was because CO₂ channeling was greatly alleviated due to the CO₂-soaking process and some reservoir brine in the core plugs was mobilized by the swollen oil and then displaced by CO₂ in the second PV of CO₂ injection. Test #11 with CO₂ soaking recovered 11.05% of the OOIP in the second PV of continuous CO₂ tertiary flooding, whereas Test #10 without CO₂ soaking achieved a moderate oil RF of 6.10% in the second CO₂ injection period. In summary, CO₂ soaking helps to recover more oil in CO₂ tertiary flooding after pre-waterflooding.

4.3.3 Oil RFs of six coreflood tests

In this study, the oil RF of pre-waterflooding, the oil RFs of CO₂ flooding in the first and second PVs of injected CO₂, as well as the total oil RF of pre-waterflooding and CO₂ flooding in each CO₂ coreflood test are given in Table 4.4. These oil RFs in different oil recovery stages of each test are also summarized and compared in Figure 4.12. It is seen from this figure that CO₂ soaking and pre-waterflooding substantially increase the total oil RF. More specifically, a significant oil RF is achieved in the second PV of CO₂ injection after CO₂ soaking, which is in the range of 11.05–14.74%. The oil RF increases only slightly in the second PV of CO₂ injection without CO₂ soaking, which ranges from 0.77% to 6.10%. It is also worthwhile to note that the oil produced in the second PV of CO₂ injection was much lighter than the oil produced in the first PV of CO₂ injection in terms of its physicochemical properties (e.g., density, viscosity, and molecular weight) and carbon number distributions under the miscible conditions [Cao and Gu, 2013b]. Furthermore, the oil RFs of pre-waterflooding in Tests #10 and #11 are
Figure 4.12  Measured oil RFs of pre-waterflooding, CO$_2$ flooding in the first PV of CO$_2$ injection, and CO$_2$ flooding in the second PV of CO$_2$ injection in Tests #6–11.
relatively high but still much lower than those of CO$_2$ secondary flooding in Tests #6–9. This fact indicates that in general, waterflooding is far less effective than CO$_2$ flooding to recover the light crude oil in tight sandstone formations. There is still a large potential for CO$_2$-EOR after pre-waterflooding. On the other hand, the total oil RFs of pre-waterflooding and CO$_2$ tertiary flooding in Tests #10 and #11 are always higher than those of CO$_2$ secondary flooding in Tests #6–9, which means that CO$_2$ tertiary flooding is rather effective to recover the water-trapped residual oil after pre-waterflooding. The mobility of the subsequently injected CO$_2$ is effectively controlled by the previously injected water. Thus CO$_2$ BT in CO$_2$ tertiary flooding is delayed and there are longer and stronger mutual interactions between the reservoir fluids and injected CO$_2$. Among all the six coreflood tests with different production schemes tested, Test #11 (pre-waterflooding plus CO$_2$ tertiary flooding with CO$_2$ soaking) achieves the highest oil RF by successfully combining the mobility-control effect of pre-waterflooding and CO$_2$-soaking effect together. Thus it is recommended to conduct the pre-waterflooding at the beginning and then the soaking process in the middle of CO$_2$ tertiary flooding in the field applications.
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This thesis study analyzed the mutual interactions between the light oil/reservoir brine and CO₂, experimentally determined the optimum timing for miscible CO₂-EOR after waterflooding, and examined soaking effect on miscible CO₂ flooding in a tight sandstone formation, the major conclusions that can be drawn from this study are listed as follows:

- The saturation pressure \( P_{\text{sat}} \) is increased from 4.97 to 8.44 MPa and the oil-swelling factor (SF) of CO₂-saturated light oil is increased from 1.14 to 1.34 when CO₂ concentration in CO₂-saturated light oil is increased from 38.94 to 60.46 mol.%;
- The gas–oil ratio (GOR) of CO₂-saturated light oil was approximately six times of the gas–water ratio (GWR) of CO₂-saturated reservoir brine under the same test conditions;
- Accordingly, the viscosities of CO₂-saturated light oils with 38.94 and 60.46 mol.% CO₂ concentrations at the saturation pressures and the reservoir temperature of \( T_{\text{res}} = 53.0 \, ^\circ\text{C} \) are lower than 16% and 10% of that of the original dead light oil at the atmospheric pressure and the same reservoir temperature, respectively;
- The equilibrium interfacial tension (IFT) between the light oil and CO₂ was about one third to one tenth of that between the reservoir brine and CO₂, which led to a much higher capillary number between the light oil and CO₂ under the actual reservoir conditions;
- The pore volumes (PVs) of CO₂ breakthrough (BT) were considerably delayed in the tests with pre-waterflooding due to a more favourable mobility ratio between the
subsequently injected CO₂ and the initially injected reservoir brine in CO₂ tertiary flooding than that between the injected CO₂ and the light oil in CO₂ secondary flooding. A larger PV of CO₂ BT indicated longer and stronger interactions between the reservoir fluids and CO₂;

- The total oil recovery factor (RF) of waterflooding and CO₂ flooding in terms of the original-oil-in-place (OOIP), the oil RF of CO₂ flooding in terms of the residual-oil-in-place (ROIP), and PV of CO₂ BT from the beginning of CO₂ flooding all reached the largest values in the intermediate waterflooding case. The optimum timing for starting the miscible CO₂ tertiary flooding after waterflooding was when the secondary oil RF of waterflooding reached half of its maximum value;

- The oil RF is increased if a lower injection rate of CO₂ is used due to a longer retention time between the reservoir fluids and injected CO₂ in CO₂ secondary flooding without CO₂ soaking;

- The average pressure inside the reservoir core plugs decreases quickly at the beginning of CO₂ soaking and reaches a relatively stable value after CO₂ soaking for 24 h. The average pressure decay during CO₂ soaking is the smallest in pre-waterflooding plus CO₂ tertiary flooding with CO₂ soaking. This is because of an increased water saturation in the reservoir core plugs and a much lower GWR of CO₂-saturated reservoir brine than GOR of CO₂-saturated light oil under the same test conditions;

- An increased production pressure leads to an increased oil RF of CO₂ flooding due to stronger mutual interactions between the reservoir fluids and injected CO₂ in the CO₂-soaking and CO₂-flooding processes; and
The oil RF of CO₂ flooding in the second PV of CO₂ injection in CO₂ secondary/tertiary flooding with CO₂ soaking is over 10%, which is considerably higher than that in CO₂ secondary/tertiary flooding without CO₂ soaking. This fact indicates that CO₂ soaking-alternating-gas (CO₂-SAG) injection is effective to recover oil from a tight sandstone formation. The mobility-control effect of pre-waterflooding and the CO₂-soaking effect jointly lead to a high oil RF of pre-waterflooding plus CO₂ tertiary flooding with CO₂ soaking.

5.2 Recommendations

Based on this thesis study, the following recommendations for future studies are made:

- Comprehensive economic analysis should be conducted to determine the optimum timing for CO₂-EOR after waterflooding in a tight sandstone formation. The optimum timing for CO₂-EOR after waterflooding should be determined not only from the total oil RF but also in terms of the overall project cost and the pay-back time. The capital and operating costs for CO₂ flooding will include CO₂ acquisition, transportation, storage, and compression, which are much higher than the cost for conducting waterflooding;

- Visualization method (e.g., X-ray scanning) can be applied to visualize the waterflooding and CO₂ flooding processes. The viscous fingering of CO₂ flooding, waterblocking effect, molecular diffusion in CO₂ soaking process, and residual reservoir fluid saturations can be visualized and analyzed;

- A mathematical mass-transfer model can be built to study the CO₂ soaking process in a tight oil formation. The molecular diffusion of CO₂ into the light oil and
reservoir brine in a tight formation is affected by the residual reservoir fluid saturations, initial soaking pressure, reservoir temperature, soaking time, fluid and reservoir characteristics. It will be beneficial to develop a comprehensive mass-transfer mathematical model that can predict the pressure decay in the CO\textsubscript{2} soaking process; and

- Mutual interactions between the light oil and CO\textsubscript{2} through water phase under reservoir conditions can be further studied to understand the waterblocking effect and the oil recovery process of the residual oil trapped by the reservoir brine. The interfacial tension between the light oil and water phase, the wettability of the rock surface, and the physical properties of the oil and brine will be changed in this CO\textsubscript{2} molecular diffusion process. Several factors, such as brine salinity, thin water film thickness, and properties of porous media, should be considered.
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