

**INVESTIGATION OF THE IMPACT OF SALINITY ON ASPHALTENE
PRECIPITATION DURING WAG-CO₂ INJECTION
FOR A MALAYSIAN LIGHT OIL**

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**PETROLEUM ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
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by

Nik Mohammad Fadhlan bin Nik Kamaruddin

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

SEP 2012

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
University Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
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Approved by,

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Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NIK MOHAMMAD FADHLAN BIN NIK KAMARUDDIN

ABSTRACT

This project aims to study the impact of low and high injection water salinity on asphaltene precipitation during WAG-CO₂ injection. Dynamic core flooding experiments were conducted with injection water salinity of 5000ppm and 35000ppm at 1:1 WAG ratio.

Dynamic core flooding experiments were conducted using Berea sandstone core as formation representative. Dulang Malaysian light crude sample with 0.39 % wt initial asphaltene content was used. 2 runs of experiments were conducted using low and high salinity of injection water at 5000ppm and 35000ppm. Secondary water flooding were conducted followed by WAG-CO₂ injection. WAG-CO₂ injection procedure from Jiang et al.(2010) will be use as a reference in this research. In WAG injection scheme, a 0.25PV half slug size of CO₂ is injected followed by 0.25PV half slug size of injection water for a total of 6 alternate cycles.

All experiment parameters were fixed at 2500psia overburden pressure and 98°C with an injection rate of 0.4cc/min (for secondary water flooding and WAG injection) and 2000psi injection pressure. The effluent oil was collected for every cycle of WAG injection (total of 6 samples). Asphaltene precipitations in the core were determined from the change in asphaltene content of effluent oil. The effects of asphaltene precipitation in the core sample were observed from initial and final porosity and permeability measurement of the core sample.

The experiment results concluded that higher brine salinity will give a higher oil recovery, lower asphaltene precipitation and lower porosity & permeability reduction.

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CHAPTER 1

INTRODUCTION

1.1 Project Background

Water alternating gas injection (WAG) had been a popular method in enhanced oil recovery (EOR) phase for reservoir which are in tertiary stage of production. Adyani et al. (2001) describes two other major types of CO₂ injections processes which are continuous CO₂ injection (CGI), and CO₂ huff 'n' puff injection.

WAG injection is popular because it improves the sweep efficiency of gas injection EOR by using water to control gas mobility. Caudle and Dyes in 1958 was originally proposed miscible gas-water injection which shows that miscible simultaneous gas-water injection yields a higher sweep efficiency than conventional water or gas injection. Simultaneous water-gas injection process contributed a total of 53% oil in place recovered at breakthrough and 98% was obtained when two reservoir volumes were injected. In the other hand, a conventional gas injection only yields 42% of oil in place at breakthrough and 62% when two reservoir volumes were injected (Caudle and Dyes, 1958). However, a later field review by Christensen, Stenby, and Skauge (2001) suggested that water and gas to be injected alternately in most field trials in USA, Canada, and former USSR countries in either miscible and immiscible condition. WAG-CO₂ injection are affected by several factors such as rock wettability, fluid properties, miscibility condition, and other WAG parameters (water-gas slug size, and WAG ratio) (Jiang, Nuryaningsih, & Adidharma, 2010).

1.2 Problem Statement

CO₂ injection in light oil reservoir will induce asphaltene precipitation. Extensive field and laboratory data confirmed that asphaltene precipitates more easily in light oil than in heavy oil even though heavy oil contains a higher asphaltene content (Sarma, 2003). Hence, Malaysian light crude oil would be a good candidate for this project. The effect of injected water salinity in WAG-CO₂ injection scheme on asphaltene precipitation had not been fully

studied in recent laboratory works and publications. Thus, this project vital to get a better understanding on asphaltene precipitation behavior since the failure of early diagnosis will result in a catastrophic wellbore, formation, and facilities problems.

1.3 Objectives

- To address the effect of high salinity and low salinity on asphaltene precipitation during WAG-CO₂ injection.
- To investigate the effect of asphaltene precipitation during WAG-CO₂ on rock properties.

1.4 Scope of study

Dynamic core flooding experiment were conducted using Berea sandstone core as formation representative. Dulang Malaysian light crude sample with 0.39 % wt initial asphaltene content was used. 2 runs of experiments were conducted using low and high salinity injection water of 5000ppm and 35000ppm. Secondary water flooding were conducted followed by WAG-CO₂ injection. WAG-CO₂ injection procedure from Jiang et al.(2010) will be use as a reference to conduct this study. A 0.25PV half slug size of CO₂ is injected followed by 0.25PV half slug size of injection water for a total of 6 cycles under 1:1 WAG ratio.

All experiment parameters were fixed at 2500psia overburden pressure and 98°C with an injection rate of 0.4cc/min (for secondary water flooding and WAG injection) and 2000psi injection pressure. The effluent oil was collected for every cycle of WAG injection (total of 6 samples). Asphaltene precipitation in the core were determined from the change of asphaltene content of effluent oil and initial oil sample. The effects of asphaltene precipitation in the core sample were observed from initial and final core properties measurement (porosity and permeability).

1.5 The relevancy of the project

EOR method is the current direction of Malaysian oil field since most of the fields are classified as matured field. PETRONAS had conducted an EOR screening in year 2000 and the outcome of the study is that the incremental recovery from EOR implementation in Malaysia oil fields is about 1Bstb (Samsudin, Darman, Husain, & Hamdan, 2005). In addition, EOR techniques that are being proposed are CO₂ and WAG injection. Therefore, this project is significant since this experimental studies of low and high salinity water on asphaltene precipitation will give a better understanding on asphaltene precipitation in field applications .

CHAPTER 2

LITERATURE REVIEW

A literature review is conducted to understand the basic properties of asphaltene mechanism of precipitation. In addition, this review aims to relate the effect of salinity on WAG recovery and CO₂ solubility in water on asphaltene precipitation.

2.1 Asphaltene in general

"Asphaltene" is firstly introduced by a French scientist, Boussingault in 1837 who used it to describe certain constituents during distillation of asphalts. These substance were insoluble in alcohol but soluble in turpentine. Since these constituent resembled the parent asphalt itself in appearance. Although with continuous research and studies, determination of the actual structures of asphaltene constituents still remains a challenge.

Physically, asphaltenes are dark brown to black with no definite melting point. Asphaltene will decompose and leave a carbonaceous residues and volatile product when heated (Sarma, 2003). Asphaltenes are soluble in *n*-alkane solvents such as *n*-heptane or *n*-pentane as well as in aromatic solvents such as toluene or benzene. Two most commonly used alkanes are *n*-pentane and *n*-heptane. The precipitate formed by adding *n*-pentane to the oil is called "pentane (C5)-asphaltenes", whereas the precipitate formed by adding *n*-heptane is called "heptane (C7)-asphaltenes". The oil is considered as "asphaltenes-free" if there is no precipitate formed.

Asphaltene precipitation is different from flocculation and deposition but all of them can induce a catastrophic formation damage in the reservoir. Precipitation of asphaltene can be divided into three processes. Firstly, precipitation starts to happen when the solid particles formed a distinct phase from the solution. Secondly, small solid particles clump together and grows. This process is called flocculation. Thirdly, as the solid particles flocculates until the particles become so large that the liquid can no longer support it and thus settle down on solid surfaces. This stage is known as deposition stage. (Alian, Omar, Alta'ee, & Hani, 2011).

2.2 Asphaltene compositions

Asphaltenes are not a pure component. Although some asphaltene species have a similar solubility behaviour but may have different chemical structures, sizes, and shapes. Asphaltene species share some common features. They are polynuclear aromatics, heteroatoms and traces of heavy metals. A study on the elemental composition of asphaltenes extracted from various crude oils around the world, Table 2.2(Speight, 1999) . Typically asphaltene molecule contains sulphur as thiophenes, thiols, sulphides, disulphides and oxidized forms. Nitrogen can exist as pyrroles and pyridines structures while Oxygen has been identified in carboxylic, phenolic and ketonic locations, and metals (nickel and vanadium) are present as porphyrins.

Table 1 : Elemental composition of asphaltenes from world sources (Speight, 1999)

	Canada	Iran	Kuwait	Venezuela
Carbon (wt%)	79.0 - 88.7	83.7	81.6 - 82.4	81.1 - 84.7
Hydrogen (wt%)	6.9 -11.1	7.8	7.8 - 8.1	7.8 - 8.3
Nitrogen (wt%)	0.7 - 2.8	1.7	0.6 - 1.7	0.2 - 2.0
Sulphur (wt%)	0.3 - 8.1	5.8	7.4 - 8.0	2.7 - 6.9
Oxygen (wt%)	0.4 - 3.9	1.0	0.6 - 1.8	1.0 - 4.2
H/C Ratio	0.98 - 1.56	1.19	1.14 - 1.19	1.13 - 1.19
N/C Ratio	0.007 - 0.029	0.017	0.008 - 0.017	0.002 - 0.02
S/C Ratio	0.001 - 0.038	0.026	0.034 - 0.039	0.012 - 0.032
O/C Ratio	0.004 - 0.037	0.009	0.005 - 0.017	0.013 - 0.039

Several standard test procedures are available for such asphaltenes extraction (ASTM D6560, ASTM D3279, ASTM D4124) in some literatures. Variations of these standard procedures have also been used (Alboudwarej et al., 2002; Kharrat et al., 2007). The part of crude oil after the removal of asphaltenes is called “deasphalted oil” or maltenes.

2.3 Problems with asphaltene precipitation

Asphaltene is not problematic as long as there is no asphaltene precipitation occurs. Formation or precipitation of organic and inorganic solids from crude oil is one of the major issues in flow assurance. Asphaltene precipitation triggers when the oil undergoes phase transitions due to changes in pressure, temperature and composition. Precipitation can lead to solid particle build-up and deposition that restrict fluid flow. The presence of precipitated solids in the oil can also change the fluid properties, such as viscosity (Alian et al., 2011).

Particle build-up is usually significant at low fluid flow rate and depends on the geometry of the flow line; for example, build-up can occur in situations where there are constrictions and expansions in the flowline. Deposition is generally affected by fluid flow rate, fluid properties (such as density, viscosity), type of solid precipitated, and adsorption of precipitated particles on to the metal surface or already deposited layer. Overall, precipitation is the first step leading to solids build-up and deposition (Tharanivasan, 2012).

In the other hand, asphaltene precipitation is more severe and is not easy to be removed as compared to wax (Alian et al., 2011). One of the example of field experience in Rainbow Key River area in Alberta, Canada had encountered asphaltene precipitation in bottom hole and surface facilities when HC gas injection are being conducted. This problems had cause a high cost on to the operator on frequent shutdowns for workover, well completions, chemical treatments with xylene and pigging of surface lines (Sarma, 2003). In addition, other remediation methods for asphaltene deposition problems include hydraulically fracturing to overcome the damaged formation near the wellbore. In a few field cases, coiled tubing with a jet attachment to remove deposits in the wellbore (Kumar et al., 2008).

2.4 Asphaltene precipitation in light oil

Asphaltene precipitation had been verified to precipitates more easily in light oil reservoir compared to heavy oil even though the heavier oil contains a higher asphaltene content. One of the field example is that, the Venezuelan Boscan crude with 17.2wt% asphaltene was produced with no asphaltene precipitation problems while the Hass-Messaoud crude in Algeria with only 0.15wt% asphaltene faced a numerous asphaltene related problems

(Sarma, 2003). This is explained by Alian et al., (2011) which concludes that although the asphaltene content in light oil is low in most cases, asphaltene content in crude oil is not the cause of asphaltene precipitation. One of the causes of this to happen is that oil with low asphaltene content have a low asphaltene solubility in the oil. Lower asphaltene solubility will increase the tendency of asphaltene precipitation to occur.

2.5 Asphaltene precipitation in WAG injection

In WAG injection scheme, the presence of water will act as CO₂ buffer. Thus, when the CO₂ gas concentration decreases as it dissolves in the water hence reducing the asphaltene precipitation. Laboratory work indicate that the presence of water film on the rock surface in water wet rock will reduces the asphaltene precipitation. Direct interaction between asphaltene and water is prevented by water shield on the surface of the rock. Therefore, a more water wet rock will give a lower asphaltene precipitation. An observation on sandstone core and limestone core shows that limestone core gives a lower asphaltene precipitation because the limestone is more water wet. (Okwen, 2006)

However, a study conducted by Tharanivasan, (2012) shows that the presence of emulsified water in oil had no discernible effects on the solubility of asphaltenes in a crude oil above the onset precipitation. However, this test does not represent the reservoir condition because the experiments were conducted at ambient pressure and temperature. In the other hand, Srivastava, Huang, & Dong (1999) agreed that the effect of brine on asphaltene flocculation are negligible but with an increase in brine salinity the asphaltene precipitation is observed to be reduces.

2.6 Effect of brine salinity on WAG recovery

There are several papers discussing on effect of brine salinity on WAG recovery (Filoco, P.R. & Sharma, M.M., 1998; Yan, W. and Stenby, E.H., 2009; Kulkarni & Rao, 2005) .The impact of injection brine salinity on WAG had been studied systematically by Jiang, Nuryaningsih, and Adidharma (2010) in a high pressure core flood system using homogeneous Berea sandstone core. The objective of their experiment is to study the effect of

injection brine salinity on oil recovery. Artificial injection brines are made by dissolving NaCl and CaCl₂ with different salinities ranging from 1000ppm to 32000ppm. They had used two types of oil in their experiments which are model oil (mixture of an equal weight of n-decane and n-hexadecane) and real crude (oil sample from Cottonwood Creek oil field). The result of their secondary recovery experiments shows that with model oil, brine salinity does not affect water flooding recovery. In the other hand, the result for secondary recovery experiment for real oil shows that an increase in injection brine salinity lowers the secondary recovery. In addition, for WAG experiments, as the injection brine salinity increases from 1000ppm to 32000ppm, WAG recovery increases from 52.8% OOIP to 59.4% OOIP in model oil and from 37% OOIP to 40% OOIP in Cottonwood Creek crude oil (Jiang et al., 2010).

2.7 Effect of brine salinity on CO₂ solubility in water

Solubility of CO₂ in injection water of different salinity had been observed to give a significant impact on oil recovery during WAG-CO₂ injection in experiments conducted by Jiang et al. (2010). An experimental studies had been conducted to study the solubility of CO₂ gas in different salinity of water (Khalid, Somerfield, Mee, & Hilal, 2007). The objective of the experiment is also aims to show the effect of temperature and pressure on CO₂ solubility in aqueous solution. From the experimental work that had been conducted, it was shown that as the system temperature increases the CO₂ gas solubility decreases in different salt solutions tested. The impact of temperature is significant in temperature between 25°C and 60°C but this effect is not clearly visible at higher temperature 80-90°C. In the other hand, the effect of system pressure on CO₂ gas solubility had shown that the CO₂ gas solubility increases when the system pressure increases from 1 to 2 bar.

Khalid et al. (2007) had also studied the effect of different type of salt solution of NaCl, MgCl₂, and Na₂SO₄. Different salts chemical structure gives a different result in CO₂ gas solubility in aqueous solution. It had been concluded that an increase in concentration of salts dissolved in water the lower the CO₂ gas solubility. The result in figure1 below confirmed that the solubility of CO₂ gas reduces with an increase in water salinity. In WAG injection, an increase in water salinity will reduces the CO₂ solubility in the water, hence more mobile CO₂ are available for the displacement of oil in the reservoir. Figure 1 also shows that at high

temperature between 80°C and 90°C which is the range of reservoir temperature, the effect of salinity on CO₂ solubility is minimal.

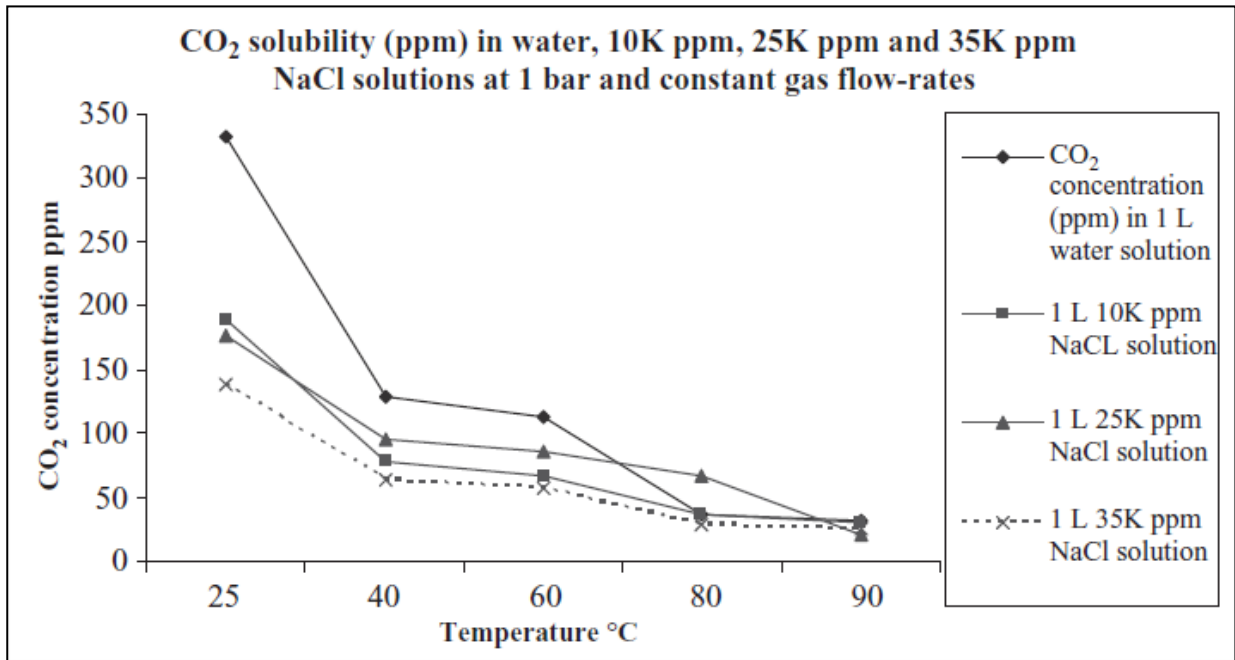


Figure 1 : CO₂ concentration at different water salinity (adapted from Khaled et al. (2007))

CHAPTER 3 METHODOLOGY

3.1 Research Methodology

In this research, dynamic core flooding will be done to study the effect of different injection brine salinity asphaltene deposition.

The generalised experimental work flow are shown in the *Figure 2* below:

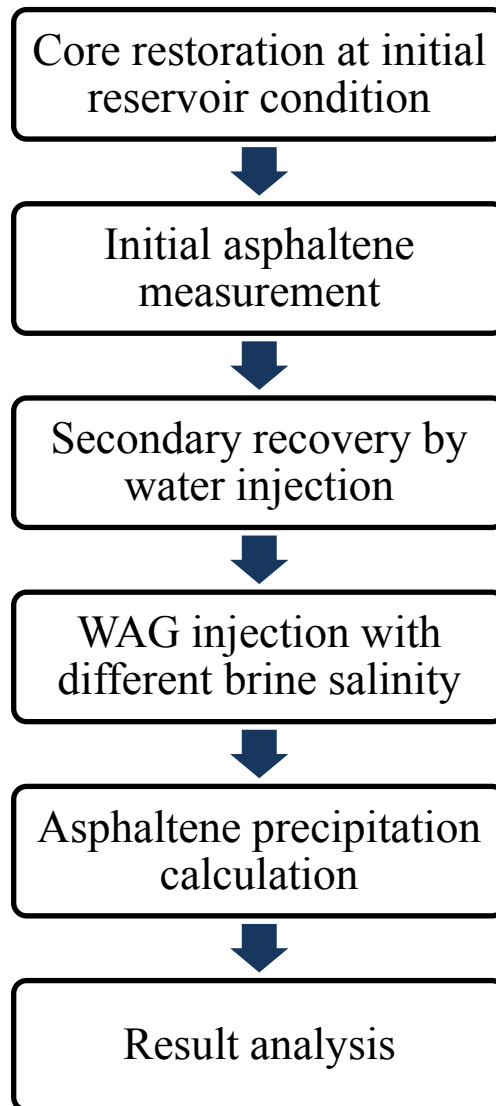


Figure 2 : Experimental work flow

Firstly, core sample is restored to initial reservoir condition. The core is saturated at 5000ppm brine to represent connate water saturation until the inlet pressure and outlet pressure is stabilised. The injection follows with crude oil injection until there is no more water is being produced followed by water injection to simulate the secondary water flooding. Initial asphaltene content is measured and recorded.

New injection brine is loaded into the fluid holder in the case of 10000ppm and 35000ppm. Secondary flooding is conducted to restore the core at residual oil saturation, injection brine is injected until no more oil is produced. Core flooding continues with WAG-CO₂ injection with 6 alternate cycles of brine and CO₂ with a half-cycle slug size of 0.25 pore volume (PV) at a WAG ratio of 1:1 in every core flood test. Oil is measured for every cycle of injection. The oil recovery was calculated.

The asphaltene content measurement of oil produced were conducted according to ASTM standard procedure D3279-07. The difference in asphaltene content of initial and final asphaltene content will determine the asphaltene weight percent precipitated in the core sample. After the WAG procedures have been completed, the core sample is then injected with n-heptane solution at 50°C and 100psia to remove the remaining oil, leaving behind the asphaltene precipitation in the core sample.

The core sample is dried in the oven for 24 hours. Final core sample porosity and permeability is measured to compare for any changes resulted from asphaltene precipitation. The results were tabulated and analysed.

3.2 Experimental details

The experimental procedures by Jiang et al., (2010) and Alian et al. (2011) will be use as a reference in this research.

3.2.1 Required Materials:

Carbon dioxide gas will be use in this WAG injection experiment. Artificial injection brine with salinities of 5000ppm and 35000ppm will be used in this experiment. Malaysian light oil from Dulang field and homogeneous Berea sandstone will be use for this core flooding experiment.

Table 2 : List of material for the project

Materials	Description
Carbon dioxide	(99.99% purity)
Brine	Artificial brine of (5000ppm, and 35000ppm) with NaCl.
Malaysian Dulang crude	This crude is selected because of low initial asphaltene content which is suitable for this project.
n-Heptane	For asphaltene measurement content experiment.

3.2.2 Required Equipments:

The core flooding will be conducted using Helium Porosimeter (Poroperm). For Asphaltene measurement, ASTM D3279 - 07 Standard Test Method for n-Heptane insoluble will be use. Helium Porosimeter, Poroperm is used to measure the core properties.

3.3 Experimental Procedures

3.3.1 Core Properties Measurement

Helium Porosimeter, Poroperm was used to determine the porosity and permeability of core sample at 300 psi confining pressure. This measurement is vital to determine the pore volume injection during secondary and WAG injection.

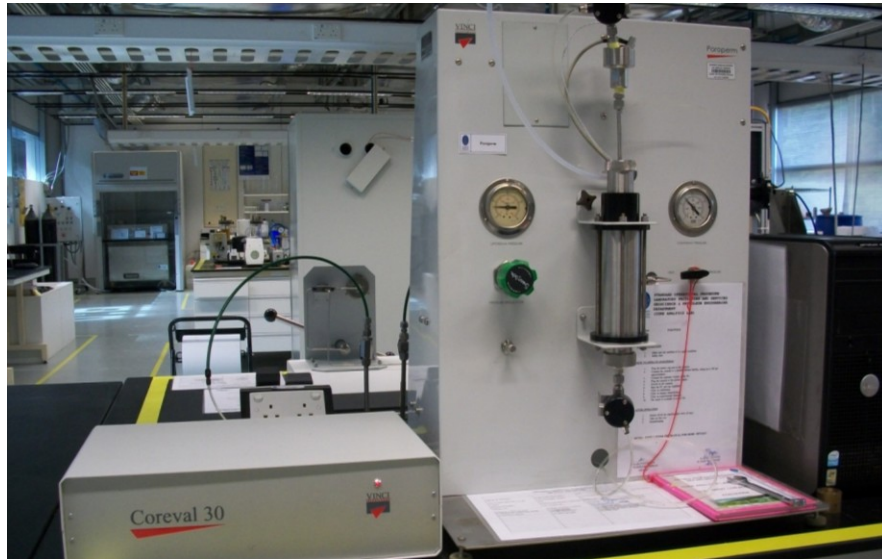


Figure 3 : Helium porosimeter, Poroperm

- i. Berea sandstone core were cleaned with toluene and dried in oven for at least 24 hours.
- ii. The length and diameter of samples were measured with digital calliper and subsequently bulk volume was determined by using formula:

$$V_b = \pi \left(\frac{d}{2} \right)^2 \times l$$

where by:

V_b = bulk volume

d = core diameter

l = length of core sample

- iii. Core sample is loaded into the core holder. Helium gas is injected through the core sample until fully saturate.
- iv. Confining pressure of 300 psi is used to obtain the porosity, K absolute, and K air.

3.3.2 Core flooding

TEMCO RPS-800-10000 HTHP, Relative permeability test system is used to conduct the dynamic core flooding experiment. Brine, oil, and CO₂ are injected simultaneously into the core sample for WAG injection experiment.

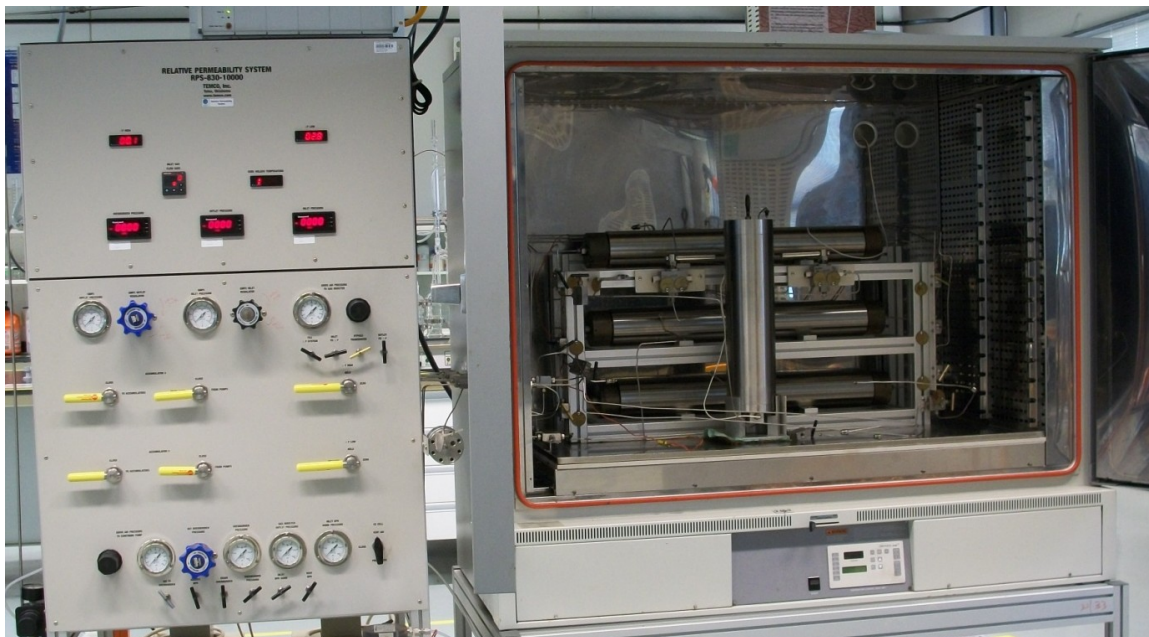


Figure 4 : TEMCO RPS-800-10000 HTHP, Relative permeability test system

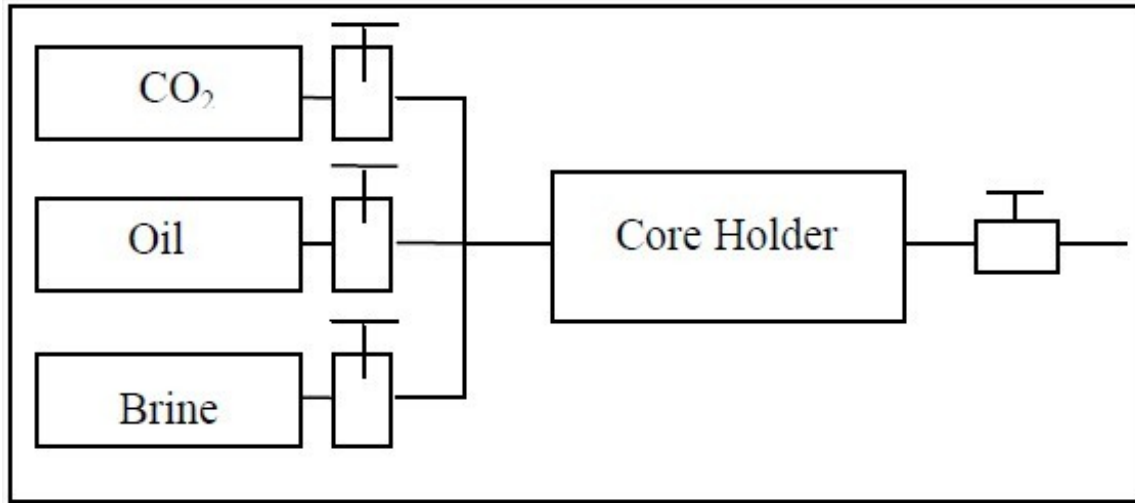


Figure 5 : Schematic configuration of core flooding system (Adapted from Jiang et al.,2010)

- i. The core sample was flooded with brine followed by dead oil for irreducible water saturation restoration.
- ii. It was assumed that the core was 100% saturated with water, where the initial volume of water should be equal to the pore volume. The original oil in place was determined through the amount of water displaced.
- iii. The core was then flooded with brine and the amount of produced oil was measured to obtain the residual oil saturation. The process was conducted until a stable residual oil was established. This is when only water is being produced at the outlet.
- iv. WAG-CO₂ injection starts to represent the tertiary recovery. 0.25PV of half slug CO₂ is injected into the core sample followed by 0.25PV of brine for a total of 6 cycles. The amount effluent oil were collected every cycle of injection to obtain the recovery factor and phase saturation change.
- v. The above step was repeated for 35000ppm water salinity WAG injection under same injection rate and conditions.
- vi. The asphaltene content in initial and effluent oil were measured according to the ASTM D3279 -07 Standard Test Method for n-Heptane insoluble.

3.3.3 Asphaltene Content Measurement

ASTM D3279 -07 Standard Test Method for n-Heptane insoluble was applied for asphaltene content measurement for initial and effluent oil from WAG-CO₂ injection.



Figure 6 : Apparatus for ASTM D3279 -07 Standard Test Method for n-Heptane insoluble

- i. Using 250ml Erlenmeyer flask, oil sample is weighted to nearest 1.0g.
- ii. 100ml of n-Heptane was added per 1.0 g of sample into the heating flask.
- iii. The flask is connected to the reflux condenser and heated at 70°C. The heating time starts when the first drop of condensed vapour from reflux condenser comes out. The mixture is heated for 20 minutes.
- iv. The mixture is cooled at room temperature for 1 hour. Glass-fiber filter pad was placed on the gooch crucible and placed in the oven at about 107 °C for 15 minutes. The gooch crucible was allowed to cool down in desiccator and the weight was measured to the nearest 0.1mg.
- v. The gooch crucible was pre-filtered with n-heptane and the mixture in the heating flask was poured into the suction flask through the gooch crucible.
- vi. The gooch crucible was put into oven for the second time at about 107 °C for 15 minutes. The gooch crucible was then allowed to cool down in desiccator and the weight was measured.
- vii. The mass percent of normal-heptane insolubles, NHI (weight percent of asphaltene content) is calculated using the formula:

$$NHI, \% = \left(\frac{m_i}{m_t} \right) \times 100$$

whereby,

m_i = total mass of insolubles

m_t = total mass of sample

3.4 Project milestone

Table 3 : Project Gantt chart and key milestones

	FYP I													
WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Activities														
Project Scope Validation	■	■												
Preliminary Report Submission		■	■	■	■									
Submission of Extended Proposal						■								
Feasibilities study on types different experimental approach						■	■							
Identifying the most suitable experimental approach						■	■	■	■					
Proposal Defense								■	■					
Submission of Interim Draft Report													■	
Submission of Interim Report														■
Lab Booking														■

	FYP2													
WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Activities														
Materials preparation	■	■	■											
1st core flooding run				■										
2nd core flooding run					■									
Post measurements					■	■	■	■	■					
Progress report submission										■				
Asphaltene analysis											■	■		
Draft report submission												■	■	
Dissertation Submission														■
Technical Paper Submission														■
Oral Presentation														■
Dissertation Submission (Hardbound)														■

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sample properties

4.1.1 Crude oil properties

Malaysian light oil from Dulang field is being used in this project. The initial asphaltene content, static & dynamic viscosity of the oil, and density is obtained from Alian et. al (2011) paper. The asphaltene contents after WAG-CO₂ injection will be compared with the initial asphaltene content to determine the amount of Asphaltene that is precipitated in the core sample.

Table 4 : Crude oil properties

Asphaltene content (wt%)	0.42
Viscosity (Cst)@98C	1.51
Viscosity (Cp)@98C	0.80
Density (g/cm)@98C	0.52

4.1.2 Core properties

Core properties such as porosity and permeability are measured using Helium Porosimeter system. Table 2 shows the core samples properties before the displacement test.

Table 5 : Core samples properties

Parameter	Core 1 (5000ppm)	Core 2 (35000ppm)
Diameter (mm)	38.10	36.82
Length (mm)	71.3	71.8
Weight (g)	174.83	164.32
Bulk Volume (cc)	81.32	76.48
Pore Volume (cc)	13.8	14.089
Kair (mD)	62.141	66.037
K _∞	56.819	60.381
Porosity (%)	16.970	18.421

4.2 Core Displacement Test

Dynamic core flooding has been conducted with a different injection brine salinity of 5000ppm & 35000ppm for both secondary water flooding and WAG injection. Table 3 represents the core displacement test parameters during water flooding and WAG injection. The confining pressure is set at 2500psi and temperature of 98 °C are use to represent the initial reservoir condition. Injection rate of 0.4cc/min at 2000 psi were applied. Injection pressure is set to be below the minimum miscible pressure (MMP) of 2957 psia to simulate immiscible WAG injection (Juan S.L., 2012). The WAG injection was conducted with 0.25PV of CO₂ followed by 0.25PV of brine for a total of 6 alternate cycles (Jiang et al., 2010). The slug size is fixed by fixing the injection time of each fluid. Oil samples were taken for each cycles of injection.

Table 6 : Core Displacement Test Parameters

Injection rate (cc/min)	0.4
Injection pressure (psia)	2000
Confining Pressure (psia)	2500
Temperature (°C)	98
WAG injection	
Total Brine injection (PV)	1.5
Total Gas injection (PV)	1.5

4.3 Result discussions

4.3.1 Oil recovery from Secondary and WAG injection

Oil recovery is defined as the percentage of oil produced from the original oil initially in place (OOIP). Currently, 2 dynamic core flooding have been conducted using 5000ppm and 35000ppm injection brine. Table 7 and table 8 summarize the result of oil recovery from secondary and WAG injection for both experimental run of 5000ppm WAG and 35000ppm WAG. Secondary flooding yields a total of 20.8% recovery and 23.26% recovery for 5000ppm and 35000ppm water salinity respectively. The difference in recovery from both cases is 2.46% OOIP which is not very significant.

This result matches with the results by Jiang et al., (2010) in figure 8 and figure 9 which obtained the same trend of results for secondary water flooding.

In WAG-CO₂ injection, oil recovery were at 28.5% of OIIP and 34.2% OIIP for 5000ppm and 35000ppm WAG respectively. The increase in recovery between 2 cases are at 5.7% of OIIP. The trend of the results matches with the trend obtained by Jiang et al. (2010). Jiang et al., (2010) used two different oil sample of Synthetic oil (Figure 8) and Cottonwood Creek Oil (Figure 9) which gave the trend of increasing WAG recovery as salinity of water increase. However, the WAG injection that had been conducted by Jiang et al., (2010) is miscible WAG where by the injection pressure is higher than MMP. Thus, the mechanism of oil displacement will be slightly different compared to this research.

The incremental recovery from WAG injection can be explained in term of CO₂ solubility in brine. In the case of high salinity brine, the solubility of CO₂ in brine will reduces thus there will be more CO₂ gas available to sweep the residual oil which explains an increase in WAG recovery.

Table 7 : Initial saturations, residual saturations and Secondary water recovery

Parameters	Injection brine salinity (ppm)	
	5000ppm	35000ppm
Pore Volume (cc)	13.8	14.089
Initial Oil Volume	9.47	8.47
Initial Oil Saturation	0.686	0.601
Initial Water Volume	4.33	5.619
Initial Water Saturation	0.314	0.399
Water Flooding		
Oil produced (cc)	1.97	1.97
Residual Oil Volume (cc)	7.50	6.50
Residual Oil Saturation	0.54	0.46
Residual Water Volume (cc)	6.30	7.59
Residual Water Saturation	0.46	0.54
Oil Recovery (%)	20.80	23.26

Table 8 : Volume of oil collected and Oil recovery for each cycle of WAG injection

Cycle	Fluid	PV	Injection brine salinity (ppm)			
			5000ppm		35000ppm	
			Volume oil collected (cc)	Oil Recovery (%)	Volume oil collected (cc)	Oil Recovery (%)
1	CO2	0.25				
	BRINE	0.25	-	-	-	-
2	CO2	0.25				
	BRINE	0.25	-	-	-	-
3	CO2	0.25				
	BRINE	0.25	0.3	3.2	-	-
4	CO2	0.25				
	BRINE	0.25	0.3	3.2	-	-
5	CO2	0.25				
	BRINE	0.25	0.8	8.4	0.1	1.2
6	CO2	0.25				
	BRINE	0.25	1.3	13.7	2.8	33.1
Total			2.7	28.5	2.9	34.2

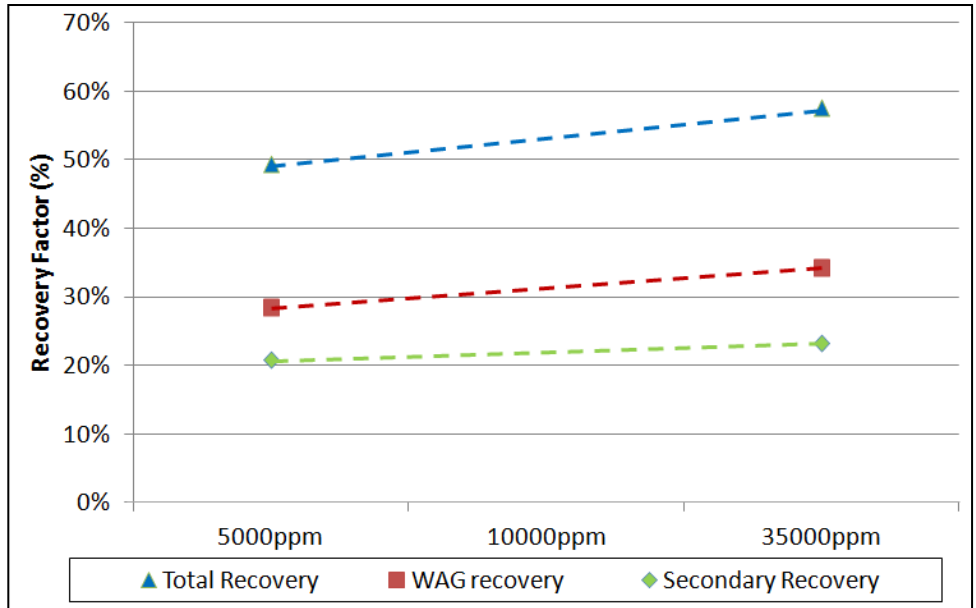


Figure 7: Recovery factor for secondary flooding and WAG injection vs Brine salinity

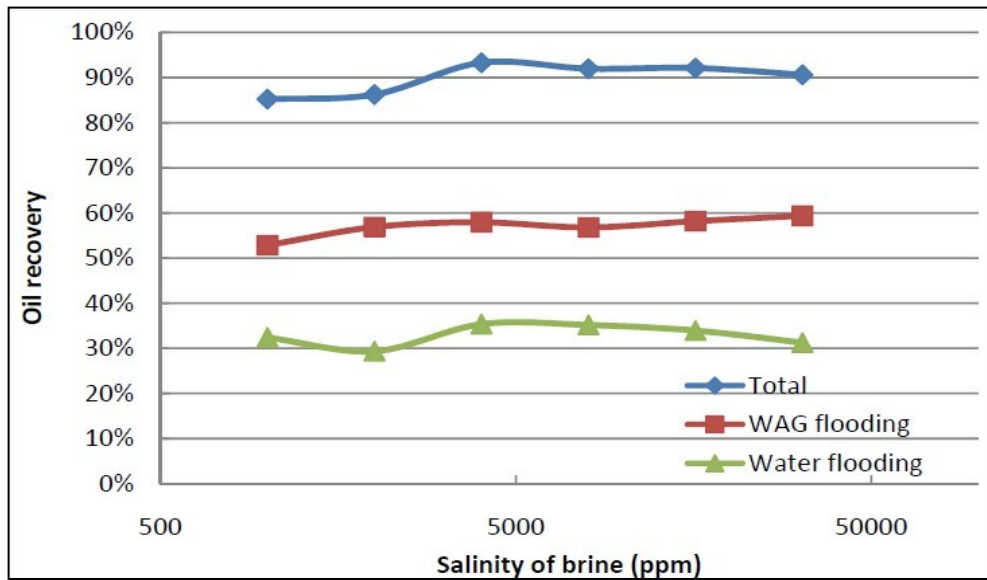


Figure 8: Plot of Oil recovery at different injection brine salinities of 1000ppm - 32000ppm for synthetic oil(adapted from Jiang et al., 2010)

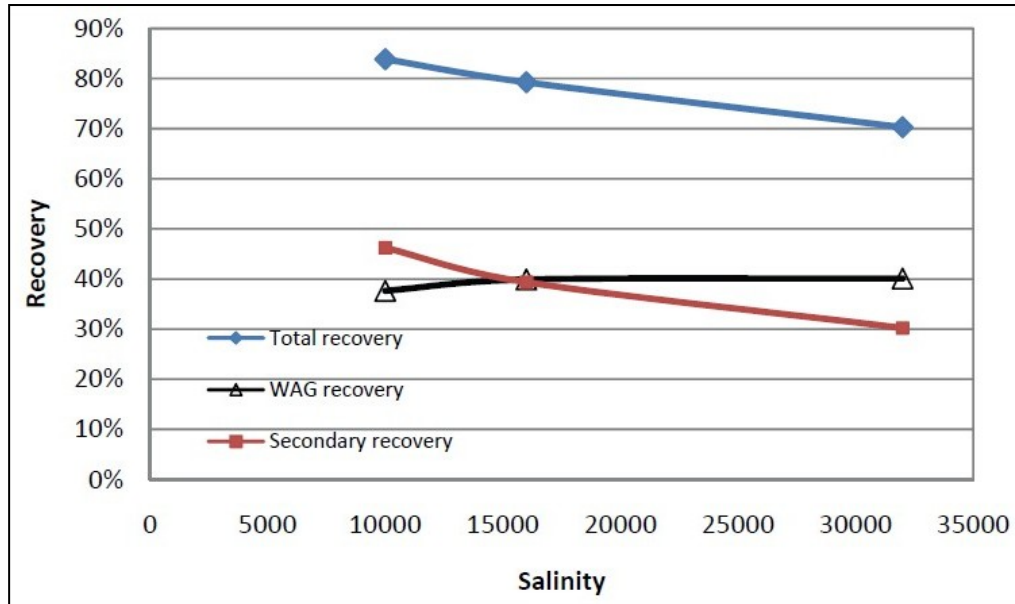


Figure 9: Plot of Oil recovery at different injection brine salinities of 1000ppm - 32000ppm for Cottonwood Creek crude oil (adapted from Jiang et al., 2010)

In the case of asphaltene precipitation, from the experimental results an increase in injection brine salinity increases the CO₂ availability for oil displacement, thus more CO₂ interaction with oil will occur. Hence it is expected that as the water salinity increases the asphaltene precipitation will also increase. However, in the experiment by Jiang et al. (2010) shows an increase in oil production does not give an indication of a lower asphaltene precipitation since the oil sample that are being use is syntethic crude oil and cottonwood creek crude oil which have an asphaltene content of 2.5 wt%. In addition, the experiment done by Jiang et al. (2010) is under high pressure thus the solubility of asphaltene is higher.

4.3.2 Asphaltene Precipitation in WAG Injection

The presence of CO₂ induces the Asphaltene flocculation followed by precipitation and deposition. Figure 10 shows the Asphaltene content of the effluent versus pore volume of injection. Oil samples are collected for every cycle of injection (0.25PV CO₂ followed by 0.25PV injection water). 2 oil samples are recovered in WAG 35000ppm and 4 oil samples are collected during WAG 5000ppm. The weight percentage

of asphaltene in effluent oil were measured based on ASTM D3279-07 Standard Test Method. The original asphaltene content of the oil is 0.39%. In the case of WAG 35000ppm, only oil sample at 5th cycle and 6th cycle were measured which explains the asphaltene content of effluent oil in the graph starts to decrease at pore volume of injection of 2.5PV. During WAG 5000ppm, oil start to produce at 3rd cycle of injection until 6th cycle of injection which gives a better trend of asphaltene content for every PV of injection. As the WAG injection continues, the amount of asphaltene content in the effluent oil decreases because some of the asphaltene is precipitated in the core sample.

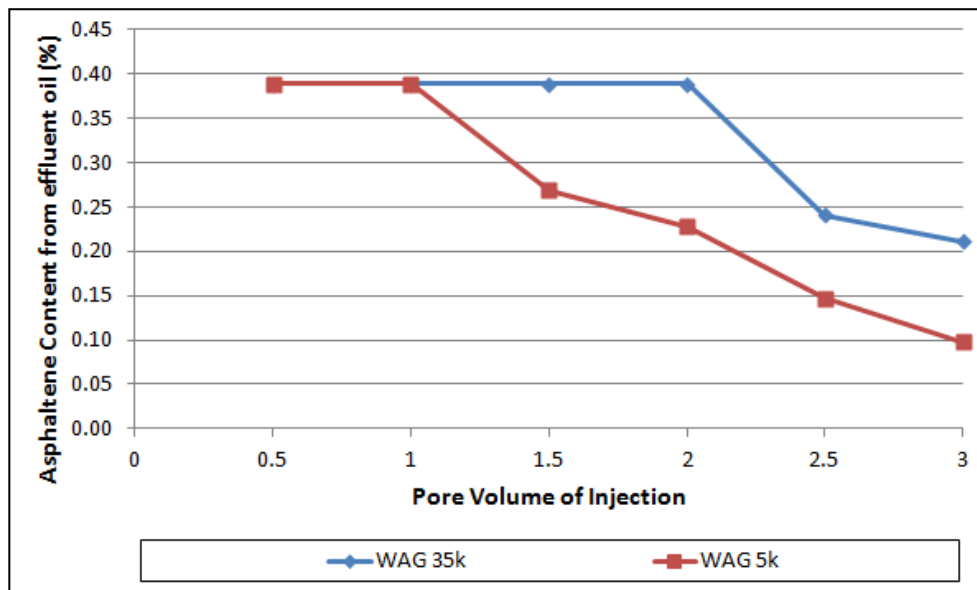


Figure 10 : Asphaltene content from effluent oil versus Pore Volume injection

Weight percentage of asphaltene precipitation inside the core sample are shown in figure 11. In WAG for 5000ppm injection water, the amount of asphaltene precipitation is 0.3085wt% at 3.0 pore volume of injected fluid while the amount of asphaltene precipitation in WAG 35000ppm is 0.2061wt% at the same injected pore volume. Based on the results, it can be observed that the asphaltene precipitation increases as the pore volume of injected fluid increases, It is also observed that a lower asphaltene precipitation is observed in high salinity WAG. This is because the higher concentration of salt ions in the water will inhibit the asphaltene precipitation on the rock.

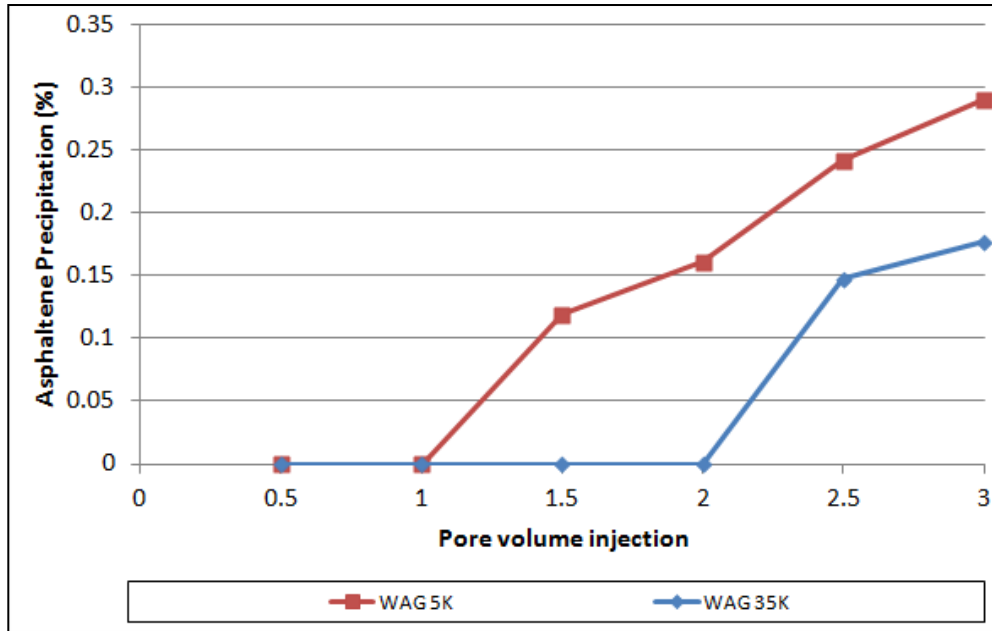


Figure 11 : Asphaltene precipitation versus Pore volume injection

4.3.3 Effect of Asphaltene precipitation on porosity and permeability

In order to determine the effect of asphaltene precipitation in the core sample, each core is injected with n-heptane solution to remove all the residual oil leaving behind only asphaltene fraction inside the core. The change of the porosity and permeability from the initial measurement indicate the extent of asphaltene precipitation. A higher porosity and permeability reduction is observed in 5000ppm WAG injection case as compared to 35000ppm WAG injection in figure 5 and 6.

Results show a high reduction in permeability for both cases which are 37.5% and 25.2% for WAG 5000ppm and WAG 35000ppm respectively. In the other hand the reduction in porosity is 8.6% and 6.7% for WAG 5000ppm and WAG 35000ppm respectively. It is confirmed that the asphaltene precipitation cause reduction in porosity and permeability of the cores. The permeability reduction is significant due to the blockage of pore throat between the sand grains. Thus the flow of the fluids are restricted and results in lower oil recovery.

The reduction in porosity and permeability were more severe in WAG 5000ppm injected water salinity. From asphaltene precipitation results, it shows that more asphaltene were precipitated in WAG 5000ppm case. Thus, it can be concluded that the reduction in porosity and permeability is proportional to the extent of asphaltene precipitation.

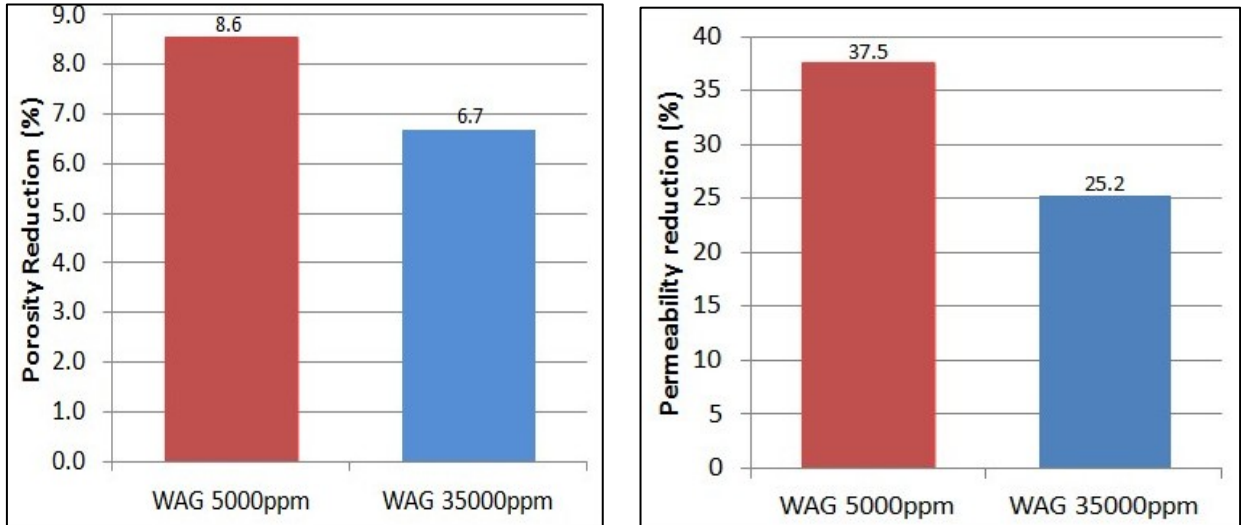


Figure 12 : Permeability and porosity reduction after WAG injection

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

WAG-CO₂ in both low (5000ppm) and high (35000ppm) water salinity induces asphaltene precipitation. The asphaltene precipitation reduces porosity and permeability of the rock. From the experimental results, a smaller reduction in asphaltene precipitation amount, porosity and permeability in high injected water salinity.

In the nutshell, it is confirmed that WAG-CO₂ injection with low salinity water induces more asphaltene precipitation than high salinity water injection as being observed in term of oil recovery, asphaltene precipitate, porosity and permeability reduction. This research will provide a better insight on WAG-CO₂ application in the field for minimal asphaltene precipitation.

Further studies on other WAG parameters such as slug size and WAG ratio as well as different gas composition and concentration can be done to get a more extensive information on optimum condition for minimum asphaltene precipitation.

REFERENCES

- Adyani, W.N., Daud, W.A.W., Darman, N., Memon, A., Khan, I.A., and Jamaluddin, A., " A Systematic Approach to Evaluate Asphaltene Precipitation during CO₂ Injection", Paper SPE 143903, SPE Enhanced Oil Recovery Conference in Kuala Lumpur, Malaysia, 19-21 July 2011.
- Alian, S.Sh., Omar, A.A., Alta'ee, A.F., and Hani, I., " Study of Asphaltene Precipitation during CO₂ injection for Malaysian Light Oil Reservoirs", Paper IEEE 978-1-4577-1884-7/11, 2011.
- Alian, S.Sh., Omar, A.A., Alta'ee, A.F., and Hani, I., "Study of Asphaltene Precipitation Induced formation damage during CO₂ Injection for a Malaysian light oil", World Academy of Science, Engineering and Technology 78, 733-737, 2011.
- Caudle, B.H. and Dyes, A.B., "Improving Miscible Displacement by Gas-Water Injection", SPE 911-G, 32nd Annual Fall Meeting of Society Petroleum Engineer in Dallas, Texas, 6-9 October 1957.
- Christensen, J.R., Stenby, E.H., and Skauge, A., "Review of WAG Field Experience", SPE 71203, revised paper 39883, SPE International Petroleum Conference and Exhibition of Mexico, Villahermose, 3-5 March 1998.
- Filoco, P.R., and Sharma, M.M., "Effect of Brine Salinity and Crude Oil Properties on Oil Recovery and Residual Oil Saturations", Paper SPE 65402, SPE Annual Technical Conference and Exhibition, New Orleans, L.A., 27-30 September 1998.
- Ganesan N., Zahidah M.Z., "Assessment of Dulang Field Immiscible Water-Alternating-Gas (WAG) Injection Through Composite Core Displacement Studies", Paper SPE 72140, SPE Aisa Pasific Improved Oil Recovery Conference in Kuala Lumpur, Malaysia, 8-9 October 2001.
- Gorrel, S.B., "Modelling the Effects of Trapping and Water Alternate Gas (WAG) Injection on Tertiary Miscible Displacement", paper SPE/DOE 17340, SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma, 17-20 April 1998.
- Jiang, H., Nuryaningsih, L., and Adidharma, H., "The Effect of Salinity of Injection Brine on Water Alternating Gas Performance in Tertiary Miscible Carbon Dioxide Flooding: Experimental Study", Paper SPE 132369, SPE Western Regional Meeting in Anaheim, California, USA, 27-29 May 2010.
- Khaled, A.A., Somerfield C., Mee D., and Hilal N., "Parameters affecting solubility of carbon dioxide in seawater at conditions encountered in MSF desalination plants", Presented at the conference on Desalination and the Environment in Sani Resort, Halkidiki, Greece, April 22–25, 2007.
- Kulkarni, M.M. (2003), "Immiscible and Miscible Gas-Oil Displacement in Porous Media". Retrieved from http://etd.lsu.edu/docs/available/etd-0709103-175151/unrestricted/Kulkarni_thesis.pdf

- Kulkarni, M.M., and Rao, D.N., "Experimental Investigation of Miscible Secondary Gas Injection", SPE 95975, SPE Annual Technical Conference and Exhibition, Dallas, TX, 9-12 October 2005.
- Kumar, P. S., van Gisberger, S., Harris, J., Ferdiansyah, E., Brady, M., Harthy, S. A., Pandey, A., "Eliminating multiple interventions using a single rig-up coiled-tubing solution", *SPE Production Operations*, **23** (2), 119-124, 2008.
- Okwen, R.T "Formation Damage by CO₂-Induced Asphaltene Precipitation', SPE paper 98180 presented at SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, 15-17 February, 2006.
- Rampersad, P.R., Ogbe, D.O., Kamath V.A., and Islam R., "Impact of Trapping of Residual Oil by Mobile Water on Recovery Performance in Miscible Enhanced Oil Recovery Processes", Paper SPE 29563, SPE Rocky Mountain Regional/Low-Permeability Reservoirs Symposium in Denver, CO, USA, 20-22 March 2012.
- Samsudin, Y., Darman N., Husain D., and Hamdan M.K., "Enhanced Oil Recovery in Malaysia: Making It a Reality (Part II)", Paper SPE 95931, SPE International Improved Oil Recovery Conference in Asia Pacific in Kuala Lumpur, Malaysia, 5-6 December 2005.
- Sarma, H.K., "Can We Ignore Asphaltene in Gas Injection Project for Light-Oils?", Paper SPE 84877, SPE International Improved Oil Recovery Conference in Asia Pacific in Kuala Lumpur, Malaysia, 20-21 October 2003.
- Speight, J. G., *The Chemistry and Technology of Petroleum*, 3rd edition, Marcel Dekker, Inc., New York, 1999.
- Srivastava, R.K., Huang, S.S. and Dong, M "Asphaltene Deposition During CO₂ Flooding", SPE paper 59092 presented at SPE Production Operations Symposium, Oklahoma City, Oklahoma, 9-11 March, 1997.
- Tharanivasan, A.K. (2012), *Asphaltene Precipitation from Crude Oil Blends, Conventional Oils, and Oils with Emulsified Water* (Doctoral dissertation). Retrieved from <http://www.ucalgary.ca/theses/%202012%20PhD%20Thesis%20Asok%20Tharanivasan.pdf>
- Yan, W. and Stenby, E.H., " The Influence of CO₂ Solubility in Brine on CO₂ Flooding Simulation", Paper SPE 124628, SPE Annual Technical Conference and Exhibition, New Orleans, L.A., 4-7 October 2009.

APPENDIXES

Table 9 : Results for Asphaltene content measurement in initial and effluent oil.

Oil Sample	B	Weight initial	Weight after	A	Asphaltene content (wt%)	Asphaltene in the core (wt%)	PV injected
Initial Oil	1.543	19.812	19.816	0.004	0.2592	-	
Initial Oil	1.03	19.402	19.406	0.004	0.3883	-	
WAG F1 35k 1st run	0			0	0.3883	0	0.5
WAG F1 35k 2nd run	0			0	0.3883	0	1
WAG F1 35k 3th run	0			0	0.3883	0	1.5
WAG F1 35k 4th run	0			0	0.3883	0	2
WAG F1 35k 5th run	0.083	23.1848	23.185	0.0002	0.2410	0.1474	2.5
WAG F1 35k 6th run	0.473	19.512	19.513	0.001	0.2114	0.1769	3
WAG F1 35k 6th run	0.7681	19.7831	19.7845	0.0014	0.1823	0.2061	3
WAG K6 5k 1st run	0			0	0.3883	0	0.5
WAG K6 5k 2nd run	0			0	0.3883	0	1
WAG K6 5k 3rd run	0.1115	19.3723	19.3726	0.0003	0.2691	0.1193	1.5
WAG K6 5k 4th run	0.1319	19.7849	19.7852	0.0003	0.2274	0.1609	2
WAG K6 5k 5th run	0.341	19.8855	19.886	0.0005	0.1466	0.2417	2.5
WAG K6 5k 6th run	0.613	23.1881	23.1887	0.0006	0.0979	0.2905	3
WAG K6 5k 6th run	0.2505	23.1843	23.1845	0.0002	0.0798	0.3085	3

B = Weight of oil sample

A = Weight of asphaltene precipitate

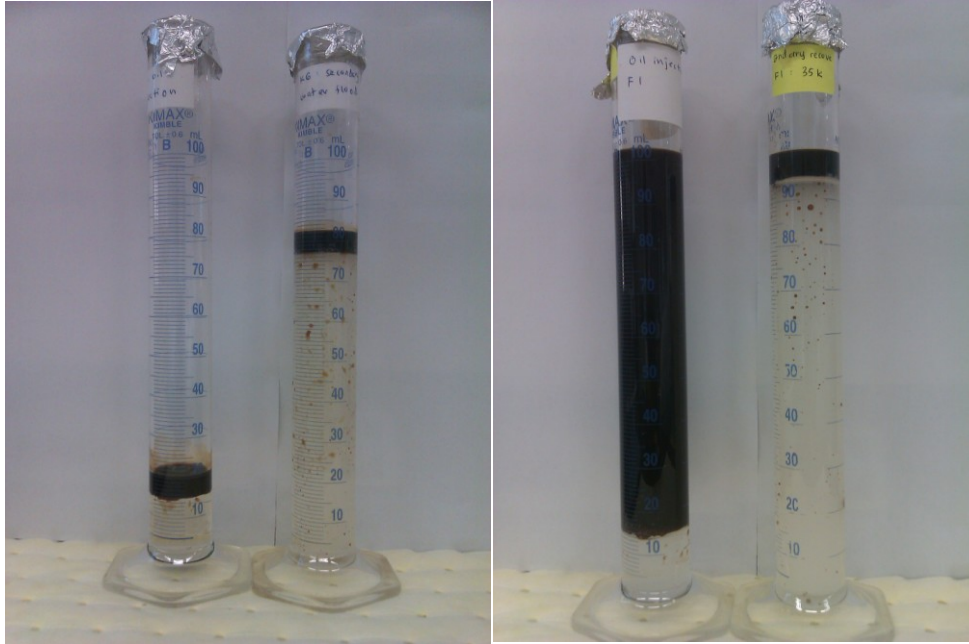


Figure 13 : Oil produced from initial oil injection and secondary water flooding.

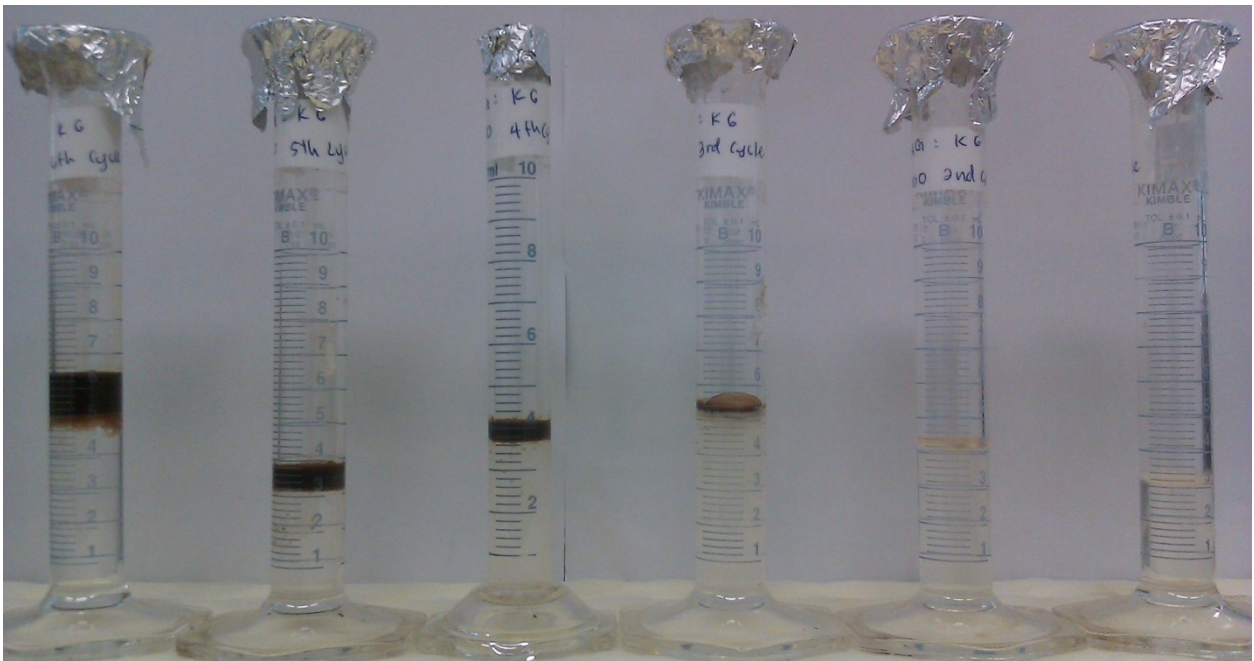


Figure 14 : Oil sample collected after each cycle of injection during 5000ppm WAG. The 1st cycle is from the right.

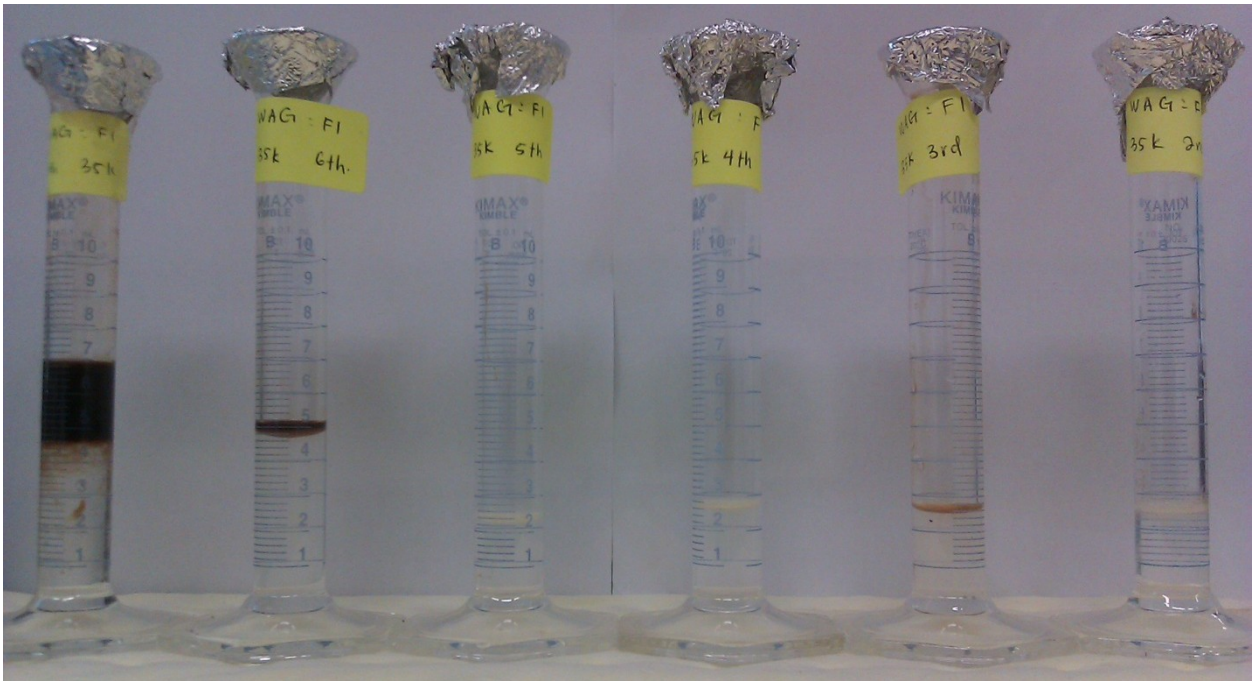


Figure 15 : Oil sample collected after each cycle of injection during 35000ppm WAG. The 1st cycle is from the right.



Figure 16 : Asphaltene precipitates on glass fiber filter paper