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Immiscible and miscible gas-oil displacements in porous media

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IMMISCIBLE AND MISCIBLE GAS-OIL DISPLACEMENTS IN POROUS MEDIA

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NOMENCLATURE

N_{ca} = Capillary Number.

V = Velocity (ft/D or cm/min)

μ = Kinematic Viscosity (cP)

σ = Interfacial tension (dynes/cm)

θ = Contact angle (degrees)

k = Permeability (effective / relative) (mD)

L = Length (cm)

Q = Flow Rate (cc/sec)

A = Cross Sectional Area (cm^2)

ΔP = Pressure Drop (psi)

L = length (cm)

M = Mobility Ratio

T = Temperature (^oF or ^oR)

MMP = Minimum Miscibility Pressure (psi)

EVP = Extrapolated Vapor Pressure(psi)

Y_{CL} = Mole percent Methane and Nitrogen

UF_{CO2} = CO_2 Utilization Factor

TRF = Tertiary Recovery Factor

S_{WC} = Connate Water Saturation (%)

S_{OR} = Residual Oil Saturation (%)

P_{TEST} = Test pressure (psi)

OOIP = Original Oil In Place (bbl)

ROIP = Residual Oil In Place (bbl)

PV = Pore Volume (cc)

IMM. = Immiscible Flood

MIS. = Miscible Flood

CGI = Continuous Gas Injection

WAG = Water Alternating Gas

S_L = Liquid Saturation (%)

S_G = Gas Saturation (%)

S_{GC} = Connate Gas Saturation (%)

MCF = Thousand Std. Cubic Feet (ft^3)

MCM = Multiple Contact Miscible

FCM = First Contact Miscible

ABSTRACT

Gas Injection is the second largest enhanced oil recovery process, next only to thermal processes used in heavy oil fields. To increase the extent of the reservoir contacted by the displacing fluids, the gas is generally injected intermittently with water and this mode of injection, called water-alternating-gas (WAG), is being widely practiced in the oil fields.

This experimental study is aimed at evaluating the performance of the WAG process in short and long cores as a function of gas-oil miscibility and brine composition. This performance evaluation has been carried out by comparing oil recoveries from WAG injection with those from continuous gas injection (CGI).

Miscible floods were conducted at 2500 psi and immiscible floods at 500 psi using Berea cores, n-Decane and two different brines, namely the commonly used 5% NaCl solution and another being the multicomponent reservoir brine from the Yates reservoir in West Texas. Each of the ten corefloods consisted of a series of steps including brine saturation, absolute permeability determination, flooding with oil (drainage) to initial oil saturation, end-point oil permeability determination, flooding with brine (imbibition) to residual oil saturation, end-point water permeability determination, and finally, tertiary gas injection to recover the waterflood residual oil.

It was found that comparing the tertiary gas floods only on the basis of recovery yielded misleading conclusions. However, when oil recovery per unit volume of gas injection was used as a parameter to evaluate the floods, miscible gas floods were found to be more effective (recovering 60-70% more oil) than immiscible floods. The WAG mode of injection out-performed the CGI floods. At increased volumes of gas injection,

the performance of miscible CGI flood inspite of the high pressure of injection, approached that of the low-pressure immiscible floods. A change in brine composition from 5% NaCl to 9.26% multivalent brine from Yates reservoir showed a slight adverse effect on tertiary gas flood recovery due to increased solubility of CO_2 in the latter. While immiscible WAG floods in short cores did not show appreciable improvement over CGI immiscible floods, the WAG flood recovery was about 31% higher than CGI floods in 6-ft Berea cores. The results of this study prompted a new process by combining CGI and WAG modes of gas injection. Such a process was found to be patented and practiced in the industry.

In addition to providing performance characteristics of the WAG process, this study has indicated directions for further research aimed at improving oil recovery from gas injection processes.

CHAPTER 1

INTRODUCTION

1.1 Background

About 377 million barrels of oil remains trapped in discovered reservoirs after primary and secondary recovery processes. This oil can be our energy source for years to come. However, as of date, this oil is deemed *unproducible* by current technology. Large research expenditure and efforts are being directed towards enhancing the recovery of this oil but with limited success. Although complete recovery of all the trapped oil is difficult, the target resource base is very large. Of the major contending processes for this trapped resource, gas injection appears to be an ideal choice.

The National Petroleum Council (NPC) defines Improved Oil Recovery (EOR) as "…incremental oil that can be economically produced…over that which can be economically recoverable by conventional primary and secondary methods". The main goals of any EOR method are increasing the capillary number and providing 'favorable' (M < 1.0) mobility ratios.

The capillary number is defined as the ratio of viscous to capillary forces.

$$N_{ca} = \frac{ViscousForces}{CapillaryForces} = \frac{v\mu}{\sigma \cos\theta} \quad \text{……………………………………………………}(1)$$

Where v and μ are the velocity and viscosity, respectively of the displacing fluid, σ is the oil-water interfacial tension and θ is the contact angle between the oil-water interface and the rock surface.

The mobility ratio, M, is defined as the ratio of mobility of the displacing fluid to that of the displaced fluid.

$$M = \frac{(k/\mu)_{Displacing}}{(k/\mu)_{Displaced}} \qquad \ldots\ldots(2)$$

Where k and μ are the relative or effective permeability and viscosity, respectively.

The overall efficiency of any Enhanced Oil Recovery (EOR) process depends on both the microscopic and macroscopic sweep efficiencies. While the fluids density difference and rock heterogeneity affect the macroscopic efficiency, the microscopic displacement efficiency is influenced by the interfacial interactions involving interfacial tension and dynamic contact angles.

Gas injection is the second largest process in enhanced oil recovery processes today[(1)]. The residual oil saturations in gas swept zones have been found to be quite low, however, the volumetric sweep of the flood has always been a cause of concern[(1)]. The mobility ratio, which controls the volumetric sweep, between the injected gas and displaced oil bank in gas processes, is typically highly unfavorable due to the relatively low viscosity of the injected phase. This difference makes mobility and consequently flood profile control the biggest concerns for the successful application of this process.

These concerns led to the development of the Water-Alternating-Gas (WAG) process for flood profile control. The higher microscopic displacement efficiency of gas combined with the better macroscopic sweep efficiency of water significantly increases the incremental oil production over the plain waterflood. The WAG process, first proposed by Claudle and Dyes in 1958, has remained the industry default mobility control method for gas injection, mainly due to the lack of proven flood profile control alternatives. Reservoir specific parameters such as wettability, interfacial tension, connate water saturation and gravity segregation add complexity to the design of a successful WAG flood. Hence the current project was initiated with the following objectives.

The important contribution of this study would be to *experimentally* demonstrate the effects of reservoir rock-fluids interactions, effects of brine composition and the development of miscibility in both continuous and WAG mode floods. Thus, this work would form the basis for the development and optimization of the proposed new gas injection process that can be used as an effective alternative to the conventional WAG process.

1.2 Objective

This experimental study is directed towards the study of the WAG process, performance as a function of several variables including the effects of brine composition and the relative merits and demerits of the miscible process over the immiscible process in both continuous gas injection and WAG floods at selected reservoir conditions in both short (1-foot) and long (6-feet) Berea cores.

1.3 Method

In order to accomplish the proposed objectives, core-flooding experiments were conducted in both 1-ft and 6-ft long Berea sandstone cores, using n-Decane as “oleic” phase and brines of two different compositions (5% NaCl brine and Yates synthetic brine) as aqueous phases along with pure CO_2 as the injectant gas. Both continuous gas injection and WAG floods were conducted. These experiments were conducted in both miscible as well as in immiscible modes.

Oil recoveries were monitored in these floods to evaluate the effectiveness of WAG process against continuous gas injection in miscible and immiscible cases in both long and short cores.

CHAPTER 2

LITERATURE REVIEW

The main aim of this project is to study the flooding characteristics of water-alternating-gas (WAG) and continuous gas injection processes in relatively homogeneous Berea sandstone cores. The continuous injection EOR process is classified under the WAG processes as a WAG process with 0:1 WAG ratio. A comprehensive review of the literature on the WAG process is presented in this section.

2.1 Mobility Control Process

The overall efficiency of the EOR process depends on both, the microscopic as well as the macroscopic sweep efficiencies. Specifically, the mobility ratio controls the aerial sweep in the reservoir, and the vertical sweep is controlled by the difference in the densities of the injected and displaced fluids. The low residual oil saturations in swept zones, and overall poor volumetric reservoir sweep are the main concerns in a gas flood. The 'unfavorable' mobility ratio in gas floods being the main cause, flood profile control in gas floods is instrumental for a successful project.

Continuous research efforts are being made to improve the flood profile control in gas floods[2][3]. These include preparation of direct thickeners with gas-soluble chemicals like Telechelic Disulfate, Polyflouroacrylate and Flouroacrylate-Styrene copolymers, which can increase the viscosity of gases several folds (e.g. For CO_2 viscosity increase from 2 – 100 fold). Other methods such as, modifications in the injected slug such as the use of Natural Gas Liquids (NGL) instead of water for highly viscous oils in low pressure, poorly producing and unconsolidated formations are also proposed[4]. Although they seem promising on the laboratory/simulator scale, important issues like feasibility, cost, applicability, safety and environmental impact still need to be addressed[4].

Most of these process modifications are still at inception or experimental stage and are not accepted as part of the current commercial flooding technology. Moritis[4], comments on the National Petroleum Council's (NPC) survey conducted for about 27 production, 16 deepwater development and 34 developmental technologies. He predicts that gas thickeners and combustion, thermal and microbial EOR processes will have lower impact in future Research, Development and Demonstration (RD&D). New directional drilling techniques, stimulation and re-completion techniques along with reservoir characterization will be the keys for cost-effective production in the oil and gas industry.

2.2 WAG Process

Almost all the commercial miscible gas floods today employ the WAG method[1]. The WAG process is shown schematically as Figure 1 below. Gas injection projects contribute about 40% of the total US-EOR production: most of which are WAG floods. Almost 80% of the WAG flood projects in the US are reported an economic success[5].

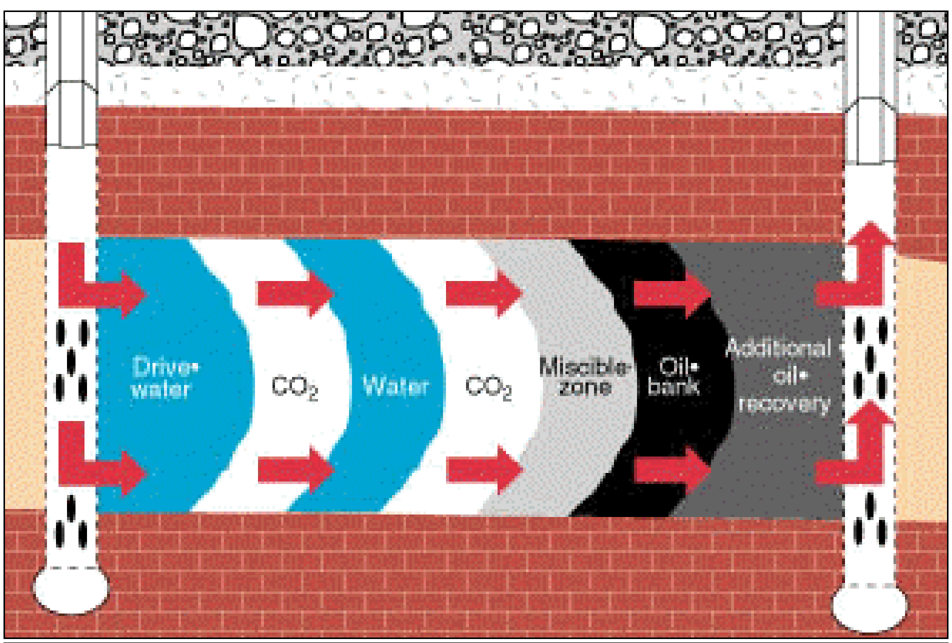


Figure 1: Schematic Of The Water-Alternating-Gas Process. (From Kinder Morgan Co.)

The WAG survey conducted by Hadlow[5] reported an ultimate recovery of about 8–14% OOIP, based on simulation and pilot tests. However, the more recent survey of 2001 by Christensen et al.[6] shows that the average increase in oil recovery was only 5 – 10%. The survey encompassed 59 projects. The popularity of the WAG process is evident from the increasing number of projects and many successful field wide applications[3].

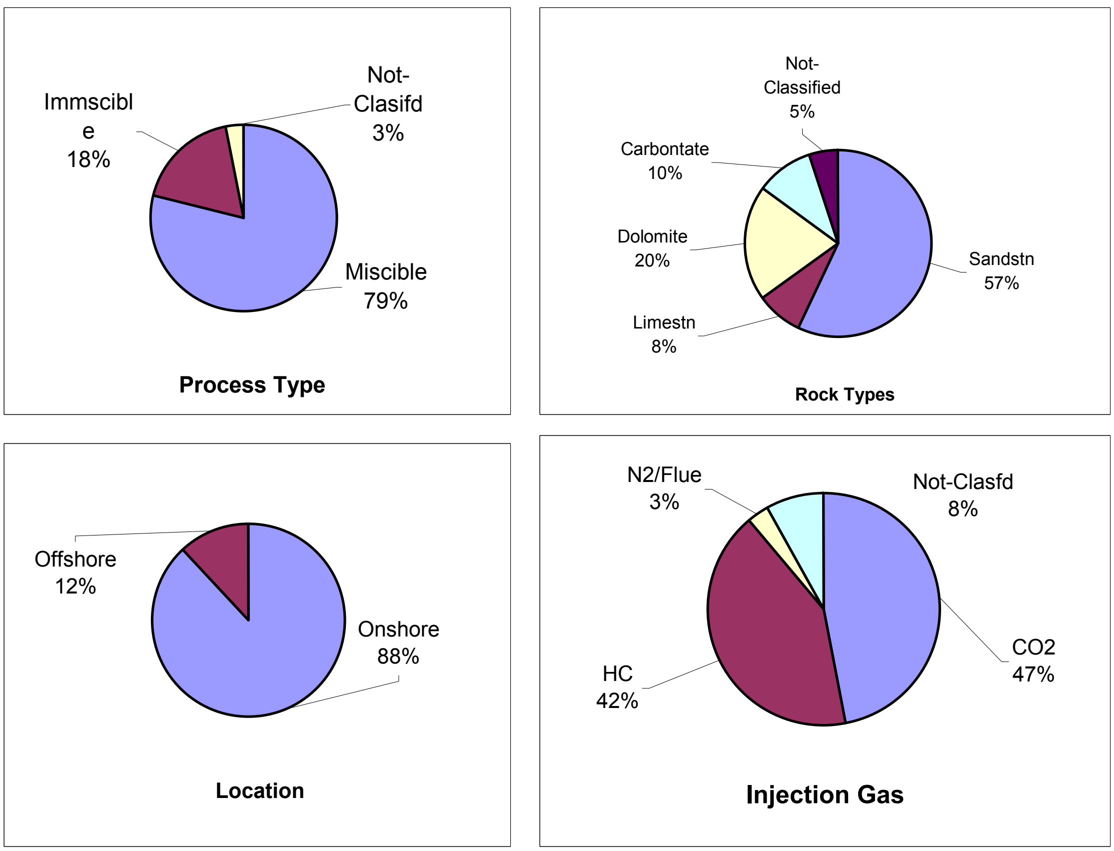


Figure 2: WAG survey – Distribution / Application of WAG (Data from Ref. 6).

The survey[6] also sheds light on the application scenario and distribution of the WAG process. US had the largest share of WAG applications of 62.7%, followed by Canada at 15.3%. The process was seen mostly applied to onshore reservoirs (88%), but applicable to a wide range of reservoir types, from chalk to fine sandstone. The popularity of the miscible flood was evident from the fact that 79% of the WAG projects employed are miscible. The CO_2 floods lead the WAG applications with a share of 47% of total projects, closely followed by hydrocarbon gas at 42%.

2.3 WAG Process Classification

The large-scale reservoir applications need a good classification system for better understanding and design of WAG process. Although Claudle and Dyes suggested simultaneous injection of oil and gas to improve mobility control, the field reviews show that they are injected separately[(6)]. The main reason for this injection pattern is the better injectivity when only one fluid is injected.

Christensen et al.[(6)] have attempted to systematically classify the WAG process. They grouped the process into four types: Miscible, Immiscible, Hybrid and Others based on injection pressures and method of injection. Many reservoir specific processes developed have been patented and are generally grouped under the 'other' WAG classification. Some of the examples are the 'Hybrid-WAG' process patented by UNOCAL[(7)], and the 'DUWAG' process of Shell[(8)]. These patented processes namely; Hybrid-WAG and DUWAG were developed to optimize recoveries from gas injection processes wherein a large slug of CO_2 is injected followed by 1:1 WAG.

2.4 Design Parameters for the WAG Process

The WAG review showed that this process has been applied to rocks from very low permeability chalk up to high permeability sandstone. Most of the applied processes were miscible. The miscibility issue is generally based on gas availability, but is mainly reported as an economic consideration and the extent of reservoir repressurization required for process application. The major design issues for WAG are reservoir characteristics and heterogeneity, rock and fluid characteristics, composition of injection gas, injection pattern, WAG ratio, three-phase relative permeability effects and flow dispersion. It is important to note that plain gas injection is considered as a part of WAG process with a WAG ratio of 0:1, hence the design issues pertinent to WAG are applicable to plain gas injection as well.

2.4.1 Reservoir Heterogeneity and Stratification

Stratification and heterogeneities strongly influence the oil recovery process. Reservoirs with higher vertical permeability are influenced by cross flow perpendicular to the bulk flow direction. Viscous, capillary, gravity and dispersive forces generally influence this phenomenon(9). Cross-flow may influence to increase the vertical sweep, but generally the effects are detrimental to oil recovery – mainly due to the gravity segregation and decreased flow velocity in the reservoir. This leads to reduced frontal advancement in lower permeability layer. WAG recoveries and continuous gas injections are more strongly affected by these phenomena. Reservoir heterogeneity controls the injection and sweep patterns in the flood. The reservoir simulation studies(10) for various k_v/k_h (vertical to horizontal permeability) ratios suggest that higher ratios adversely affect oil recovery in WAG process.

Gorell(11) reported that the vertical conformance of WAG displacements is strongly influenced by conformance between zones. In a non-communicating-layered system, vertical distribution of CO_2 is dominated by permeability contrasts. Flow into each layer is essentially proportional to the fractional permeability of the overall system (average permeability * layer thickness (k*h)) and is independent of WAG ratio, although the tendency for CO_2 to enter the high permeability zone with increasing WAG ratio cannot be avoided. Due to the cyclic nature of the WAG, the most permeable layer has the highest fluid contribution, but as water is injected it quickly displaces the highly mobile CO_2 and all the layers attain an effective mobility nearly equal to the initial value.

These cause severe injection and profile control problems. The higher permeability layer(s) always respond first. WAG will reduce mobility not only in the high permeability layer but also in the low permeability layer, resulting in a larger amount of the CO_2 invading in the highest permeability layer.

The ratio of viscous to gravity forces is the prime variable for determining the efficiency of WAG injection process and controls vertical conformance of the flood. Cross-flow or convective mixing can substantially increase reservoir sweep even in the presence of low vertical to horizontal permeability ratios. Heterogeneous stratification causes physical dispersion, reduces channeling of CO_2 through the high permeability layer, and delays breakthrough. This is attributed to permeability and mobility ratio contrasts[(9)]. This is unfavorable and greatly influences the performance of the flood. However, the effects are reservoir specific and the overall effect is dependent on various parameters like permeability, porosity, reservoir pressure, capillary pressure and mobility ratio [(9)(11-13)].

2.4.2 Rock and Fluid Characteristics

Fluid characteristics are generally black-oil or compositional PVT properties obtained in the laboratory by standardized procedures[(9)]. Very accurate determination of fluid properties can be obtained with current techniques.

However, rock-fluid interactions such as adhesion, spreading and wettability affect the displacement in the reservoir. In reservoir simulators all these rock-fluid interactions are generally lumped into one parameter – relative permeability. The relative permeability is the connecting link between the phase behavioral and transport properties of the system. Relative permeability is an important petrophysical parameter, as well as a critical input parameter in predictive simulation of miscible floods. Relative permeability data are generally measured in the laboratory by standardized procedures with actual reservoir fluids and cores and at reservoir conditions[9].

2.4.3 Injection Gas Characteristics

This issue is more related to the location than the applicability of the reservoir. The question of availability is most important as far as the design criteria are concerned. The CO_2 design criteria suggest a minimum depth limitation as well as dictate the specific gravity and viscosity criteria of the oil to be produced from the concerned reservoir. In offshore fields, the availability of hydrocarbon gas directly from production makes hydrocarbon gas injection feasible. Good example of this issue is the Ekofisk field where miscible hydrocarbon WAG was suggested to be more suitable for Ekofisk, even though CO_2 WAG yielded higher incremental production under laboratory conditions[14]. Christensen et al.[6] suggest that all the offshore fields use hydrocarbon WAG, however the option to use CO_2 is being tested for environmental concerns.

2.4.4 Injection Pattern

The WAG process review[6] clearly shows the popularity of the 5-spot injection pattern with close well spacing on shore. In spite of higher costs, the 5-spot injection pattern with closed well spacing is still popular since it gives better control over the process. Inverted 9-spot patterns are also reported in DUWAG and the Hybrid WAG projects of Shell and Unocal respectively.

2.4.5 Tapering

Tapering is the decrease in gas-to-water ratio as the flood progresses. This is generally done to control the gas mobility and channeling as well as to prevent early breakthrough of the gas. This step is important especially when the injected gas is expensive and needs recycling. Tapering is generally done in most of the CO_2 and hydrocarbon floods and prevailed even in the earliest WAG flood trials[5][6].

2.4.6 WAG Ratio

The optimum WAG ratio is influenced by the wetting state of the rock[10]. WAG ratio of 1:1 is the most popular for field applications[6]. However, gravity forces dominate water-wet tertiary floods while viscous fingering controls oil-wet tertiary floods. High WAG ratios have a large effect on oil recovery in water-wet rocks resulting in lower oil recoveries. Tertiary CO_2 floods controlled by viscous fingering had a maximum recovery at WAG ratio of about 1:1. Floods dominated by gravity tonguing showed maximum recovery with the continuous CO_2 slug process. The optimum WAG ratio in secondary floods was a function of the total CO_2 slug size.

For water-wet rocks, 0:1 WAG ratio (continuous gas injection) is suggested for secondary as well as tertiary floods[10]. For a partially oil-wet rock, tertiary gas injection with 1:1 WAG ratio is suggested. The recovery depends on the slug size with larger slug size yielding better results. A 0.6 PV slug size gives maximum recovery, but 0.2 – 0.4 PV slug size is dictated by economics. Tertiary and secondary CO_2 floods (in both oil-wet and water-wet reservoirs) are viscous (or finger) dominated[10]. In these cases, miscible CO_2 floods would greatly enhance oil recovery since miscibility reduces fingering considerably.

2.4.7 Flow Dispersion Effects

The WAG injection results in a complex saturation pattern as both gas and water saturations increase and decrease alternatively. This results in special demands for the relative permeability description for the three phases (oil, gas and water). There are several correlations for calculating three-phase relative permeability in the literature[15], but these are in many cases not accurate for the WAG injection since the cycle (water / gas) dependant relative permeability modification and application in most models are not considered. Stone II model is the most common three-phase relative permeability model used in commercial reservoir simulators today; however, it is necessary to obtain experimental data for the process planned.

2.4.8 Gravity Considerations in WAG

Green and Willhite[16] suggest that the same density difference, between injected gas and displaced oil, that causes problems of poor sweep efficiencies and gravity override in these types of processes can be used as an advantage in dipping reservoirs. Gravity determines the 'gravity segregation' of the reservoir fluids and hence controls the vertical sweep efficiency of the displacement process. Gravity-stable displacements of oil by plain gas injection or WAG in dipping reservoirs as secondary or tertiary process results in very high oil recovery. This has been confirmed by laboratory tests, pilot tests as well as field applications[1][17-24]. Although the purpose of WAG injection is to mitigate the gravity segregation effects and provide a stable injection profile, WAG in downdip reservoirs have shown better profile control and higher recoveries. Hence the gravity considerations in WAG design are indispensable.

2.4.9 Laboratory Studies and Simulation

Detailed laboratory studies coupled with reservoir simulation are of paramount importance for successful WAG design[25]. The quality of data input to the simulator is the key to provide quality predictions[26]. For compositional simulations phase behavior and slim-tube experiments should be performed and used to tune the EOS model. This tuned model helps in accurate characterization of reservoir fluid. Also relative permeability and capillary pressure hysteresis modeling for three-phase flow is a requirement when simulating miscible WAG floods. Although these compositional effects do not affect immiscible floods to the same extent as in miscible floods, a tuned EOS coupled with an accurate three-phase relative permeability model is required for reliable predictions from the simulation. Significant improvements are being made in three-phase relative permeability models[27-32]. As a result, accuracy of the simulation studies is improving.

2.5 The Need for Miscibility Development

Most of the gas injection processes could be segregated as miscible or immiscible. Gas injection processes are most effective when the injected gas is nearly or completely miscible with the oil in the reservoir[33]. The immiscible gas flood increases oil recovery by raising the capillary number due to the relatively low interfacial tension values between the oil and injected gas. In miscible flooding, the incremental oil recovery is obtained by one of the three mechanisms: oil displacement by solvent through the generation of miscibility (i.e. zero interfacial tension between oil and solvent – hence infinite capillary number), oil swelling and reduction in oil viscosity[34].

Miscible flooding has been used with or without WAG for the control of viscous fingering and reduction in gas-oil interfacial tension of the system. Miscibility is achieved by repressurization in order to bring the reservoir pressure above the minimum miscibility pressure (MMP) of the fluids. Christensen et al.[6] observed that it is difficult to distinguish between miscible and immiscible processes since in many cases a multi-contact gas-oil miscibility may have been obtained. This leads to uncertainty about the actual displacement process. Loss of injectivity and/or failure of pressure maintenance in the actual reservoir, attributable to many factors, cause the process to fluctuate between miscible and immiscible during the life of the process. The authors[5] also point out that the earlier miscible processes used expensive solvents like propane, which are uneconomical in the present price context. The injectivity problems and pressure loss dictate closer well spacing – hence increased costs – although no severe impairments in the project economics have been reported because of these problems only[5].

There seems to be no consensus in the literature for the need for development of miscibility in gas floods[33-35]. Rogers and Grigg[9] suggest that interfacial tension is the most sensitive and the most easily modified parameter in the capillary number, and suggest that considerable decrease in interfacial tension at relatively low cost is the benefit of miscible flooding. However, overlapping values of interfacial tension for immiscible, near-miscible and miscible floods have been reported[6][36][37]. Although Rogers and Grigg[9] suggest a way to improve the capillary number, the issue of viscous forces still needs to be addressed. Viscous forces strongly depend on the reservoir heterogeneities, petrophysical properties and cross-flow in the reservoir, hence are strongly reservoir dependant. Rao[36] suggests the use of chemicals to alter wettability in non-water wet reservoirs where miscibility achievement (for reduction in interfacial tension) may not be as important as the water-wet reservoirs where miscibility is useful to maximize pore-level displacement efficiency.

2.6 Effect of Brine Composition

The migration of small solid materials (‘fines’) within porous media has long been recognized as a source of potentially severe permeability impairment in reservoirs[38]. This impairment has a strong effect on the flow capability (relative permeability) of the reservoir rock. Fines migration occurs when loosely attached particles are mobilized by fluid drag forces caused by the motion of fluid within the pore space. One of the primary factors that determine the migration of clay particles is the brine composition. Laboratory studies[38] have shown that brine salinity, composition and pH can have a large effect on the microscopic displacement efficiency of oil recovery by waterflooding and imbibition.

Gray and Rex[39] in their study of the migration of mica needles and kaolinite, found that fines migration, consequently permeability reduction, could be induced by salinity changes or abrupt reductions in the ratio of divalent to monovalent ions present in the brines. Mungan[40] studied the effects of permeability reduction ('Core Damage') due to changes in pH and salinity of the injected brine. He concluded that the permeability reduction occurs, regardless of the type of clay, due to changes in brine salinity.

Capabilities of divalent cations like [Ca^{2+}] and [Mg^{2+}] to control permeability impairment of reservoir due to swelling of clays have been long recognized[39][41][42]. This phenomenon is attributable to the cation exchange properties of clays, which inherently favor the adsorption of [Ca^{2+}] and [Mg^{2+}] ions over [Na^{+}]. The clays in their calcium-form are less easily dispersed compared to the clays with sodium, and they are easily interchangeable by flowing a solution containing other cations[41].

Even though the literature is unison about the effects of brine composition on permeability reduction and fines migration, there seems to be little consensus about the effects of brine composition on oil recovery (either by waterflooding or imbibition). Kwan et al.[43], in their study of permeability damage via fines migration in extracted core material, concluded that permeability and oil recovery were nearly independent of brine composition. Contrarily, other experimental studies[41][42][44][45], suggested that changes in brine composition could have a large effect on oil recovery.

Waterflooding and core imbibition experiments conducted by Tang and Morrow[44] with 1% solutions of $NaCl$, $CaCl_2$ and $AlCl_3$ showed increased waterflood recoveries (forced displacement) and decreased (natural) imbibition rates with increase in cation valency. Generally, oil recovery increases with decrease in brine salinity[44].

In contrast to the observations of Tang and Morrow[44], Sharma and Filoco[45] conducted centrifuge experiments on Berea cores and found that oil recovery via imbibition increases significantly with increasing salinity of connate brine.

2.7 Importance of CO_2 as Injectant Gas: U.S. Perspective

CO_2 injection remains an important method for improving oil recovery in the US in-spite of oil price swings and ownership realignments. The CO_2 process leads the gas injection processes, with a contribution from Nitrogen and Hydrocarbon (HC) processes. This is especially true in the Permian basin of West Texas and New Mexico. Over 95% of the CO_2 flooding activity, accounting for 4% of total EOR production, is in the United States, and mainly in the mature Permian Basin of the southwestern US and dominated by injection under miscible conditions[4][6].

The EOR survey[49] and Moritis[50] observe that the CO_2 miscible processes are on the rise while the other gas processes, like flue gas, Nitrogen etc., seem to have become practically extinct. The lower costs for implementing CO_2 floods are due to gas processing facilities as well as large reserves of almost pure CO_2 in Mississippi, West Texas, New Mexico, Oklahoma, North Dakota, Colorado and Wyoming. These are supported with extensive CO_2 pipeline infrastructure, from CO_2 source fields and gas processing facilities. The CO_2 pipeline network is shown in Figure 3. Projected oil recoveries from these projects are in the order of 7-15% of OOIP[6][9]. Computer simulation capability and reduction in development costs have made the CO_2-based processes even more attractive in recent years.

The injectivity problems with CO_2 are less severe compared to other gases due to the higher viscosity of CO_2. Furthermore, the lower formation volume factor (FVF) of CO_2 and lower mobility ratio make the volumetric efficiency higher for CO_2 than other solvents and solvent mixtures. The CO_2 density is much closer to typical light oil density than are most other solvent injectants, making CO_2 less prone to gravity segregation compared to N_2 and CH_4. Another beneficial effect of CO_2 is the likelihood of higher gravity segregation in the high water saturation zones of the reservoir than in the higher the oil saturation zones. This effect is also useful to target pockets and bypassed areas of oil and drain them effectively[9].

The use of CO_2 emitted into the atmosphere for enhancing oil recovery has recently generated interest in both the environmental and petroleum researchers. The CO_2 sequestration has the benefit of reducing the emission of greenhouse gases and increasing oil recovery.

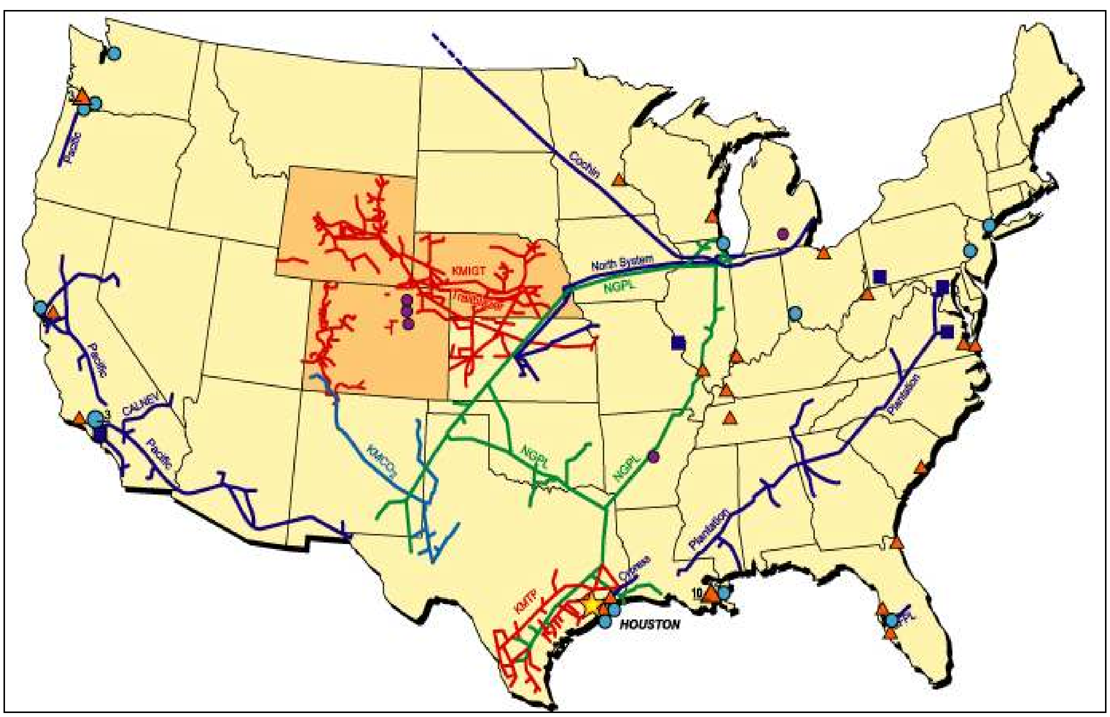


Figure 3: Extensive Network of CO_2 Pipelines in The U.S. (From Kinder Morgan Co.)

2.8 Problems Associated with the WAG Process

Although laboratory models show very high sweep efficiencies, the complexity in operations and gravity override make WAG a difficult process in the field to minimize the mobility driven instabilities associated with the gas flood processes. Decrease in sweep efficiency farther from the injection well and gravity segregation of injected gas and water are illustrated in Figure 4.

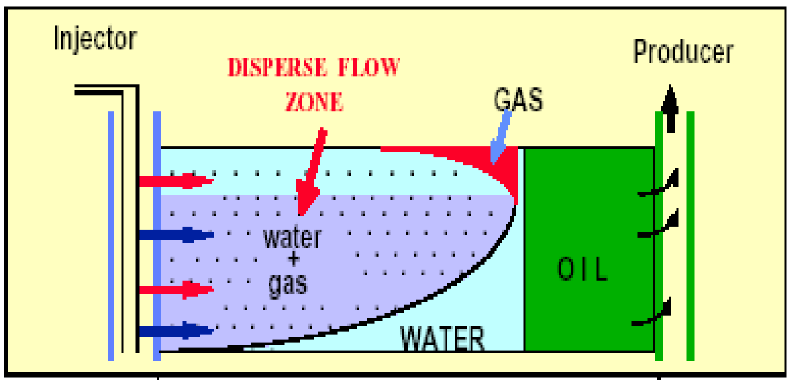


Figure 4: Schematic of The Gas-Water Gravity Segregation in Far-Wellbore Region[25]

Literature review shows that gas injection is generally applied as a tertiary flood, after a secondary waterflood. High water saturations shield residual oil from injected solvent giving rise to severe water-shielding effect in tertiary gas floods. This effect is more prominent in water-wet reservoirs. Wettability affects the water-shielding effect, which is further discussed in the literature[10][36].

Apart from these reservoir problems, there are many reported operational problems for WAG implementation like corrosion, asphaltene and hydrate formation, and early breakthrough. A complete and exhaustive list of operational problems have been described by Christensen et al.[6]. Good management and operational procedures are required to mitigate these operational problems, and "Negative effects with WAG injection are rarely seen, and most operational problems have been handled successfully[6]". Nevertheless, these procedures require close monitoring and constant update. The WAG recoveries rarely exceed 5 – 10% and major operational problems are a part of the daily routine for the operators.

2.9 Literature Review Summary

The gas injection EOR processes today contributes a substantial portion of the oil from light oil reservoirs, next only to thermal processes used in heavy oil reservoirs and their importance is continuing to rise.

Nearly all the commercial gas injection projects today employ the WAG method. The WAG process has long been considered as a tertiary gas injection mobility control process after a secondary waterflood. Previous research and field applications have repeatedly proven the inadequacy of the WAG process, yet it has remained the default process due to absence of a viable alternative. The low recoveries from the WAG process lead to substantial research of the process and consequently some of its limitations are eliminated. In spite of these improvements, the field performance of WAG process is disappointing. Hence the full utilization of EOR potential in the U.S. requires the development of new and more efficient gas injection processes that overcome the limitations of the WAG process.

In the United States, most of the WAG applications are onshore, employing a wide variety of injection gases for a wide range of reservoir characteristics in the miscible mode. Although many types of injectant gases have been used in the commercial WAG floods, CO_2 and Hydrocarbon gases form the major share of injectant types (~ 90%).

The main design parameters that need to be evaluated on a laboratory scale so as to evaluate the feasibility of the process are: Reservoir heterogeneity, rock type, fluid characteristics, injection gas, WAG ratio and gravity considerations. Other important parameters that are important for gas injection and tertiary recovery in general are those of miscibility development and oil / brine composition (characteristics).

CO_2 is ideally suited for the use as an EOR gas in the U.S. scenario. Abundance of reserves of almost pure CO_2 and availability of technical know-how can be instrumental in the growth of CO_2 injection process. Carbon sequestration is an added advantage of the CO_2 injection projects.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

The research work is directed towards an evaluation of the Water-Alternating-Gas (WAG) process. Its design parameters and rock-fluid interactions in a laboratory. This project aims to study the flooding characteristics of WAG and continuous injection processes in short and long Berea sandstone cores and to determine the effects of gas-oil miscibility and brine composition.

3.1 Tasks Identification

Coreflood experiments to identify the multiphase flow characteristics of the fluids are central to this project. The corefloods of the project are of the dynamic displacement type. Identification and separation of parameters to effectively study their effects on the process is required. Pure CO_2 gas has been used as an injectant in all the floods. n-Decane has been used as the 'Oleic' phase and two types of brine have been used as the aqueous phases to measure the effects of brine compositions (i.e. mono-valent vs. multi-valent brine).

Initially, base case flooding experiments have been conducted using Berea cores, 5% NaCl (mono-valent) brine and n-Decane. Because n-Decane is considered to be 'non-reactive' in terms of wettability effects, the data generated served as the base case for comparing water-wet system data. The base case experiments have been conducted in WAG and continuous gas injection corefloods in both miscible and immiscible modes using a horizontal Berea core system set up. Similar experiments have been conducted using n-Decane and multi-valent (Yates reservoir) brine so as to examine the results of brine composition and stability of clays. These experiments have provided the data on gas-oil displacements (both miscible and immiscible) in Berea sandstone cores for the 'non-reactive' system.

3.2 Experimental Fluids

Analytic grade reagents were used in all the experiments. N-Decane and the salts that were used for synthetic Yates brine preparation were from Fisher Scientific with a purity of 99.9%. To prepare the brines, deionized water from the Water Quality Laboratory at Louisiana State University was used. The compositions of the two brines used in the tests are shown in Table 1 below. The Berea sandstone (Liver Rock type) used in the experiments was from Cleveland Quarries, Ohio.

Table 1: Brine Compositions Used in Various Experiments

5% NaCl Brine	Pure NaCl Salt (200 gm) in 4 Liters Deionized water.	
Yates Synthetic Brine	*Salt Type*	*Weight / 4 L (gm)*
	Sodium Chloride ($NaCl$)	23.26
	Calcium Chloride ($CaCl_2.2H_2O$)	11.77
	Magnesium Chloride ($MgCl_2.6H_2O$)	8.13
	Strontium Chloride ($SrCl_2.6H_2O$)	0.26
	Barium Chloride ($BaCl_2.2H_2O$)	0.0071
	Sodium Sulfate (Na_2SO_4)	0.95
	Ferrous Ammonium Sulfate ($Fe. (NH_4).(SO_4)_2.6H_2O$)	0.028

3.3 Experimental Design

To following plan of experiments was implemented to accomplish the objectives of this study.

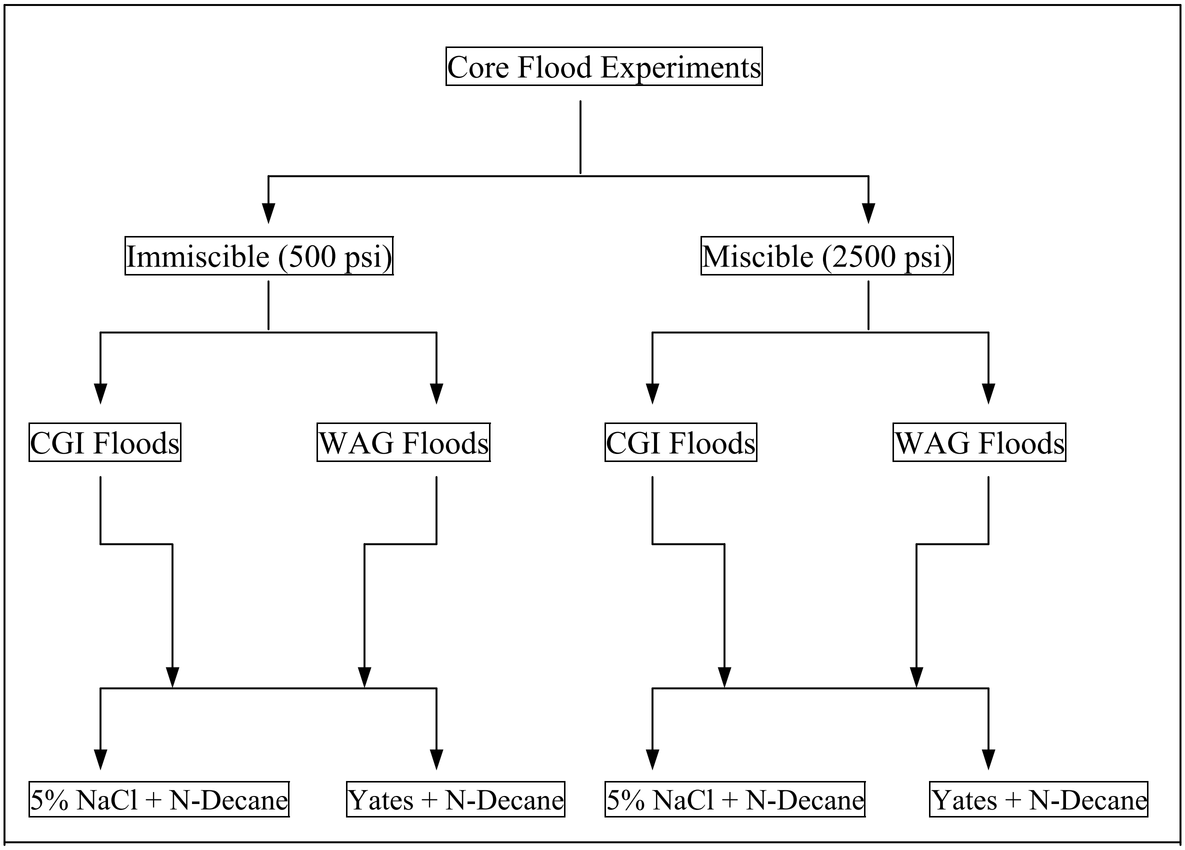


Figure 5: Design of Coreflood Experiments

Pure CO_2 was used as the injection gas in all the floods. The minimum miscibility pressure (MMP) for the fluid-pair was estimated to be approximately 1880 psi. Hence, the immiscible floods were conducted at 500 psi and the miscible floods at 2500 psi. The experiments to be conducted are:

Set A: Immiscible Floods (System Back Pressure < Minimum miscibility pressure)

- 6-ft Berea + n-Decane + 5% NaCl brine System
  1. Horizontal mode immiscible continuous CO_2 flood.
  2. Horizontal mode immiscible CO_2 – WAG flood.
- 1-ft Berea + n-Decane + 5% NaCl brine System
  3. Horizontal mode immiscible continuous CO_2 flood.
  4. Horizontal mode immiscible CO_2 – WAG flood.

- 1-ft Berea + n-Decane + Yates reservoir brine System

   5. Horizontal mode immiscible continuous CO_2 flood.

   6. Horizontal mode immiscible CO_2 – WAG flood.

Set B: Miscible Floods (System Back Pressure > Minimum miscibility pressure)

- 1-ft Berea + n-Decane + 5% NaCl brine System

   - Determination of MMP for n-Decane + CO_2 system

   1. Horizontal mode miscible continuous CO_2 flood.

   2. Horizontal mode miscible CO_2 – WAG flood.

- 1-ft Berea + n-Decane + Yates reservoir brine System

   3. Horizontal mode miscible continuous CO_2 flood.

   4. Horizontal mode miscible CO_2 – WAG flood.

3.4 Experimental Setup

The high-pressure coreflood apparatus was setup to conduct unsteady state coreflood experiments. The schematic of the apparatus is shown in Figure 6 below. It consists of a high-pressure Ruska pump injecting fresh (tap) water at desired flow rate and pressure to the bottom part of the floating piston transfer vessel. The transfer vessel is filled with the fluid to be injected into the core. High-pressure steel piping (1/8" ID) carries the fluid and is injected into the core with the assistance of a liquid re-distributor plate. The produced fluids were carried through the backpressure regulator into a measuring cylinder / electronic balance to determine fluids production as a function of run time. A parallel set of piping was constructed to facilitate the circulation of core clean-up fluids using a centrifugal pump. The inlet, outlet, differential, back and annulus pressures were measured using electronic pressure transducers (previously calibrated against a standard dead-weight tester) mounted on the coreflood apparatus.

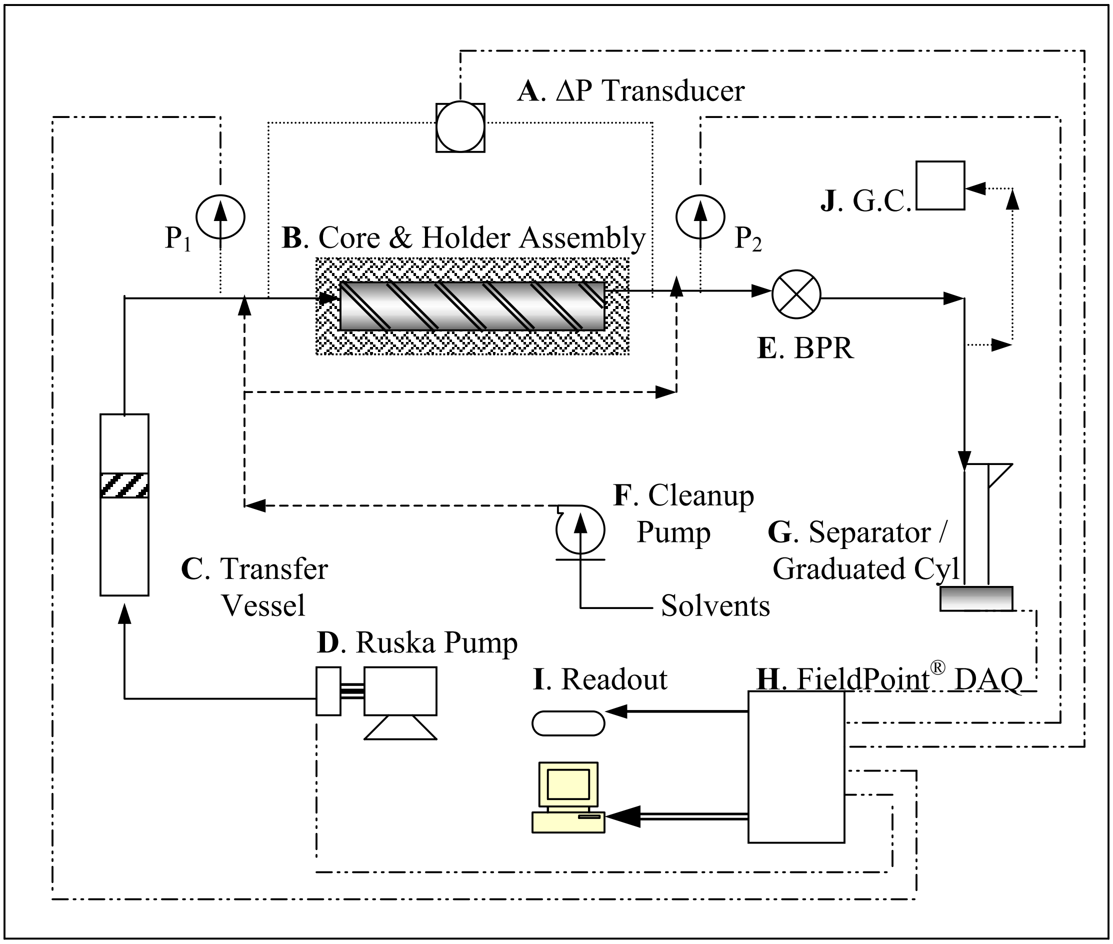


Figure 6: Horizontal Core Flooding System Schematic

Legend for the above schematic:

- .... : Electrical Lines
- ———— : 1/8" High Pressure Piping
- _.._.._.._.. : Instrumentation Lines
- ----------- : Cleanup / Accessories Lines

The vital components of the core-flooding apparatus are labeled from 'A' to 'J'. Individual pictures of the equipment are shown in Figures 7 – 17. This experimental setup used a fresh 1-ft long Berea core as the porous medium for eight of total ten tests carried out. The cores have a single coating of epoxy on them to prevent damage during handling and processing of the core such as end facing, polishing and cutting.

Figure 7: Differential Pressure Transducer (A)

Figure 8: 6-ft Berea Core with Epoxy Coating (B)

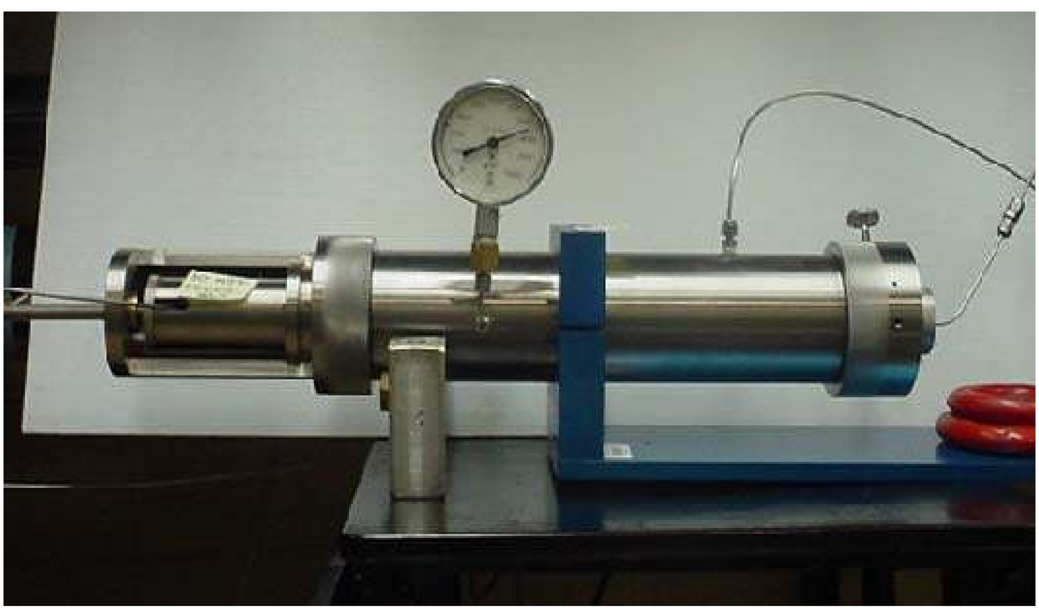


Figure 9: 1-ft Core Holder (B)

Figure 10: Fluid Transfer Vessel (C)

Figure 11: Ruska Positive Displacement Pump (D)

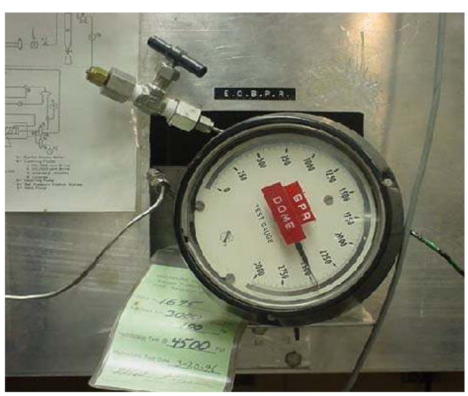


Figure 12: Back Pressure Regulator (E)

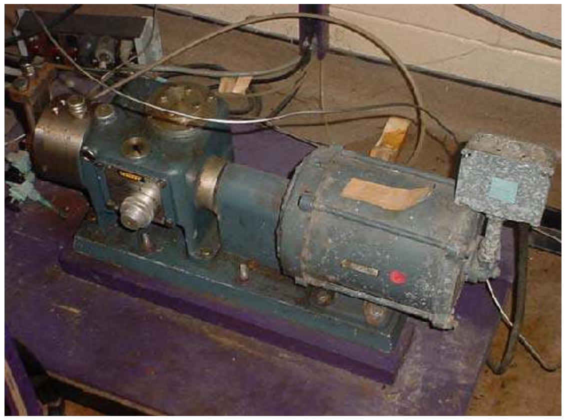


Figure 13: Cleanup Centrifugal Pump (F)

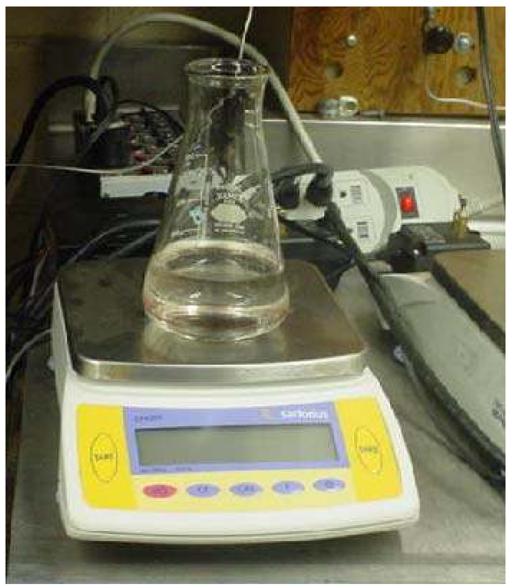


Figure 14: Electronic Balances (G)

Figure 15: Field Point Data Acquisition Hardware (H)

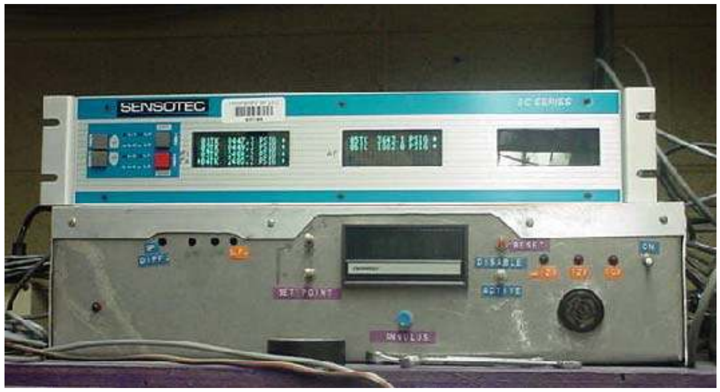


Figure 16: Pressure Readout (I)

Figure 17: Gas Chromatograph (J)

3.5 Experimental Procedure

There were two types of experiments performed. They were Continuous gas injection and WAG. All the experiments consisted of the following steps: Saturation with brine, determination of pore volume and absolute permeability, oil flood to connate water saturation, end point oil-permeability, waterflood to waterflood residual oil saturation, end point water-permeability and tertiary gas flood. The core filled with brine solution after core cleaning to determine pore volume and absolute permeability. It is brought to connate water saturation by flooding with n-Decane at high flow rates (160 cc/hr). The core is then water flooded (60 cc/hr) using the brine of similar composition as the connate water to bring the core to water-flood residual oil saturation. This is the imbibition process (Berea generally being a water-wet rock), which represents the secondary recovery process. At the end of the imbibition process, significant residual oil remains in the core. WAG injection and continuous CO_2 injection tests were then conducted after the secondary recovery process.

When two-phase flow occurs in any porous medium, capillary pressure is usually present unless the flood is miscible. The capillary pressure depends on local curvatures of the fluid / fluid interfaces, which in turn depend on saturation, saturation history, wettability and pore geometry(9)(37).

Laboratory transient-state displacement processes are affected by viscous instabilities and discontinuities at the inlet and, more importantly, the outlet of the core, which is referred to as the 'end effect'. End effects can be minimized by using large core lengths and pore volume. The scaling criterion of Leas and Rappaport(52) has been used to remove the dependence of oil recovery on injection rate and core length. The use of this scaling criterion helps the capillary pressure gradient in the flow direction to be smaller than the imposed pressure gradient. The scaling criterion is given by,

$$L.V.\mu \geq 1 \qquad (3)$$

where L is the core length (cm), μ is viscosity of displacing phase (cP) and V is fluid velocity (cm/min).

The Leas and Rappaport scaling criterion calculations were repeated for each injection fluid to ensure stable floods. The Leas and Rappaport scaling criterion value of 7.5 was used in all the corefloods conducted in this study. It is interesting to note that this criterion is generally met in the reservoir scale floods due to the large distances between injector and producer.

As stated earlier, every flood has its own unique procedure. However, common operations like cleaning and absolute permeability measurement are applicable to all floods. The final tertiary EOR process is experiment dependent. The procedure is as follows.

3.5.1 Core Cleaning Procedure

Typically at the end of any coreflood, oil, brine, and gas (CO_2) exist in the core. To begin a new coreflood experiment, it needs to be cleaned. Prior to instigating a new coreflood, an extensive cleaning procedure was followed to restore the core to a known initially strongly water-wet state. In the procedure, cleaning fluids are flooded at high rate and low pressure to save time. This step requires accurate pressure and flow rate monitoring because errors in this process may lead to improper cleaning and consequently induce errors in the test following this operation.

- At first, the core is flushed with 4 – 5 pore volumes (PV) of normal brine solution. This step is essential to completely eliminate the traces of residual gas in the core. This injection is initially conducted in one direction followed by equal amount of flushing in the normal direction.
- The salt concentration in the core is decreased by flushing with 2 – 3 PV diluted brine solution in both directions.
- The core is then flushed with 2 PV Methylene Chloride to act as a buffer between the injected brine and cleaning fluids. The buffer prevents possible contact of chemicals such as Toluene and Acetone with the brine that could cause possible precipitation of the salt and consequentially damage the core.

- This core is then flushed with 2 PV Toluene until a clear effluent is obtained and no more oil is solubilized. The high solubility of oil components of oil in toluene ensures complete removal of the residual oil in the core.
- Another slug of Methylene Chloride (~ 2 PV) is injected as a buffer between Toluene and next cleaning chemical, which was Acetone.
- About 2 PV of Acetone is injected to act as a dehydrating agent to remove traces of residual brine (if any). Acetone also helps dissolve traces of oil (N-Decane) that Toluene may have left. Now the core is free of all the fluids it contained at the start of the cleaning procedure.
- The core is then re-flushed in both directions with 2 PV Methylene Chloride until a clear effluent is obtained. Now the core is ready to be injected with brine.
- The Methylene Chloride is then dislodged from the core using a diluted brine solution in both forward and reverse directions.
- Finally normal concentration brine solution is flushed in both directions into the core.

Sufficient backpressure is maintained to ensure good core cleaning. Also the stepwise increase/decrease in brine concentration during the cleaning procedure is important to prevent any permeability impairment to the core, especially while using monovalent (5% NaCl) brine.

3.5.2 Absolute Permeability Measurement

The core is fully saturated with brine at the start of this step. The absolute permeability of the core is then measured, which also serves as a means to check the efficiency of the cleaning procedure. The procedure involves the following steps.

- Flood the core using field/synthetic brine (about 1 – 2 hrs for each flow rate) after the cleaning process is over. This step is required despite the fact the core was just flushed at the end of cleaning process with brine. This flood is performed at lower flow rates to establish pressure equilibrium and removal of any entrapped air.
- Brine flooding is continued until a stable pressure drop is obtained.
- The brine production and pressure drop are measured and tabulated.
- The procedure is repeated for three different flow rates till consistent pressure drops and permeability are obtained.
- The measured stable pressure drops and the corresponding flow rates are used to calculate absolute permeability of the core using Darcy's law,

$$k = \frac{Q.\mu.L}{A.\Delta P} \quad \text{.....(4)}$$

Where, Q is flow rate in cc/sec; μ is the viscosity of injected fluid in cP; L is the length in cm; A is the cross-sectional area in cm^2, and ΔP is pressure drop in psi.

3.5.3 Oil Flood To Determine Connate Water Saturation

The oleic phase (n-Decane) is first transferred to the oil transfer vessel and pumped into the core using the Ruska positive displacement pump. The oil must always be filtered before pumping it into the core. This is done using an in-line oil filter.

- The core was flooded using n-Decane (or Crude oil) for 2 PV.
- The volumes of brine and oil produced and pressure drop are measured and recorded as a function of time.
- The oil flood is conducted at 160 cc/hr flood rate to satisfy the Leas and Rappaport criterion.

- After 2.0 PV oil injection or till no more water is produced, whichever is later, the flow rate was changed (100 cc and 60 cc) and the system was allowed to stabilize before measuring the stabilized pressure drops.
- The measured stable pressure drop(s) and the corresponding flow rate(s) are then used to calculate end-point effective permeability of the core to oil using Darcy's law.
- The connate water saturation (S_{WC}) was then determined through material balance.

3.5.4 Secondary Brine Flood To Determine Residual Oil Saturation

Now the core is at connate water and initial oil saturation. The brine flood can be directly started after step 3.4.3. The core was aged for 24 hours for wettability restoration or refinement of the oil – water distributions at the pore level. Because n-Decane was considered to be non-reactive with little or no wettability effects, the relatively short ageing time of 24 hours was considered to be adequate.

- The core was flooded using synthetic / field brine (about 2 PV) after the oil flood.
- The volumes of brine and oil produced and pressure drop are measured and recorded as a function of time.
- The flood is conducted at 60 cc/hr flood rate to satisfy the Leas and Rappaport criterion.
- After about 2.0 PV injection, the flow rate was changed (30 cc and 10 cc) and the system was allowed to stabilize before measuring the stable pressure drops.
- The measured stable pressure drop(s) and the corresponding flow rate(s) are used to calculate end-point water permeability of the core using Darcy's law.

- The material balance was used to calculate the S_{OR}.

3.5.5 Tertiary Carbon Dioxide Gas Floods

The tertiary gas injection was carried out in two modes: continuous CO_2 injection and Water-Alternating-Gas (WAG) injection using the following procedure.

Continuous CO_2 Injection

- The core was flooded with CO_2 gas (approximately 2 PV) after the brine flood.
- The flood is usually carried out at very low flow rates to ensure stability of the floods. Flooding rate of 10 cc/hr is used to satisfy the Leas and Rappaport criterion. This being the slowest step in the overall experimental procedure, it needs careful planning and monitoring.
- The brine, oil and gas volumes produced are measured using the separator readout and gasometer or wet gas meters and tabulated as a function of time
- At the end of the CO_2 flood, the injection is continued for three different flow rates. The system is allowed to stabilize at each flow rate and then the observed pressure drop is measured. This gives the end point permeability of gas at residual liquid saturation.
- Material balance is used to calculate the S_{GC}.

Water-Alternating-Gas Injection

- The core was flooded with CO_2 and water alternately after the brine flood.
- The flood is usually carried out at relatively low flow rates to ensure stable floods. Flooding rate of 10 cc/hr was used to satisfy the Leas and Rappaport criterion. This being the slowest step in the overall experimental procedure, it needs careful planning and monitoring.

- The slug size used was 20% of the pore volume (PV). Gas and water are injected alternately in 20% PV slugs.
- It is important to have similar pressures in both the brine and gas cylinders to prevent instabilities and early breakthrough during the flood. For this brine and CO_2 transfer vessels are connected to the pump and allowed to equilibrate for at least 24 hours.
- After equilibration of pressure in both brine and gas cylinders, 20% PV slug of gas was injected into the core. An equal volume slug of brine was then injected.
- This procedure was repeated till 2.0 PV volume injection (brine and gas volumes together) is completed.
- The brine, oil and gas volumes produced are measured using the separator readout and gasometer (used in immiscible gas floods) or wet gas meters (used in miscible gas floods) and tabulated as a function of time
- Material balance was used to calculate the S_{GC}.

CHAPTER 4

RESULTS AND DISCUSSION

The main objective of this work is to determine the effects of miscibility and brine composition on three-phase displacements in Berea cores for tertiary mode gas floods. It has been experimentally shown that crude oil and other chemical additives to brine (to enhance recovery in secondary mode) have wettability effects[53]. n-Decane in this project along with two types of brine (viz. 5% NaCl brine and Yates synthetic brine) was used to isolate these wettability effects. The non-reactive (absence of wettability effects) nature of these systems has already been experimentally proven[53]. The design of experiments to achieve the proposed objectives is illustrated in section 3.2 of chapter 3.

Literature review shows wettability alterations can be inferred from the observed changes in the relative permeability curve characteristics such as S_{WC} (initial water saturation or crossover point of the curves). Craig's rules of thumb[54] were used to interpret wettability changes from the experimental results. The rules of thumb are summarized below in Table 2.

Table 2: Craig's Rules Of Thumb[54] for Wettability Interpretation.

Wettability Criterion	**Water-Wet Rock**	**Oil-Wet Rock**
Connate Water Saturation (S_{WC})	> 0.20 – 0.25 %	< 0.15
End Point Oil Permeability at Connate Water saturation ($K_{re\ (@\ connate\ water)}$)[53]	> 0.80 – 0.95	< 0.7
End Point Water Permeability at Waterflood residual oil saturation ($K_{re\ (@\ waterflood\ residual\ oil)}$)	< 0.30	> 0.50

The results are grouped according to fluid systems and further subdivided between immiscible and miscible displacements. The comparison of WAG and continuous CO_2 floods are included under their mode of displacements. To nullify the effect of reservoir / core heterogeneity on displacement characteristics in a porous medium, all the core floods are conducted on the same 1-ft Berea rock sample. The P & T, flow rates, cleaning fluids and n-Decane used for the tests are similar for all the core floods conducted. These experimental controls ensure that the core has been exposed to the same history prior to the various tertiary mode recovery tests.

4.1 Laboratory Procedural Changes

In the course of this research, the need for some new laboratory procedural changes was realized. The most important change was to use fresh Berea cores rather than the ones with a previous history of exposure to crude oil. The crude oil causes changes in the wettability of the core rendering it non-water wet, indicating lower end point oil permeabilities.

The core cleaning procedure used previously was found inefficient, and IPA (Isopropyl Alcohol) used for the water removal caused precipitation and consequential permeability reduction of the core, with 5% NaCl Brine solution. A review of literature suggested use of Toluene, Methylene Chloride, Chloroform-Methanol azeotrope and acetone for core cleaning. Chloroform-Methanol azeotrope was not considered for safety reasons and instead acetone (a strong dehydrator) was used. The core cleaning procedure was modified as toluene and acetone alternating with methylene chloride.

For all the displacement tests, the Leas and Rappaport criterion was employed to ensure stability and repeatability of the experiments. Every immiscible core-displacement experiment was conducted using two sets of reservoir fluids: 5% NaCl Brine with n-Decane and Yates Synthetic Brine with n-Decane. Continuous CO_2 and CO_2 WAG experiments were conducted using both sets of reservoir fluids. The pressure drop and recovery plots for all experiments are included as appendix A.

4.2 Minimum Miscibility Pressure (MMP) Of CO_2 / n-Decane System

The PVT simulation packages available today often do not yield predictions accurate enough to be used without any experimental verification. The volumetric and phase compositional data for various CO_2 binary mixtures available from visual cell experiments is scattered and not as useful for phase property calculations[55].

4.2.1 From Literature

Although, the utility of n-Decane and CO_2 as a potential candidate for coreflood experiments was recognized as early as 1960's, its 'minimum miscibility' data was not systematically studied. Individual researchers had their own estimates for the MMP and were used by them accordingly. This could be partially blamed on the non-standardization of the slim tube and rest on the discrepancies in the definition of 'miscible flood'.

The reservoir simulators require experimental verification and calibration to predict the phase properties with good accuracy. Orr and Silva[55], conducted continuous miscible contact experiments using n-Decane and CO_2 at 1260, 1510 and 1760 psia, however the aim of the experiment being the study molecular interactions and phase solubility's, the importance of MMP was not recognized.

Further to these studies, Orr and Jensen[56] presented and studied pressure – composition (P-X) diagrams for many CO_2/Crude-oil systems. The results indicated for low-temperature systems (below 120 ^oF), the extrapolated vapor pressure (EVP) of CO_2 is a good estimate of pressure required to produce a dense, relatively incompressible CO_2-rich phase that can extract hydrocarbons efficiently from a crude oil. Further to this, the authors report that in absence of any other experimental evidence, the EVP curve can be used as a rough estimate of the MMP for low temperature reservoirs. The phase diagram for CO_2/N-Decane (at 160 ^oF) shows that above ~ 1880 psia, single-phase mixture results. Therefore, the MMP cannot be any higher than 1880 psia for this system.

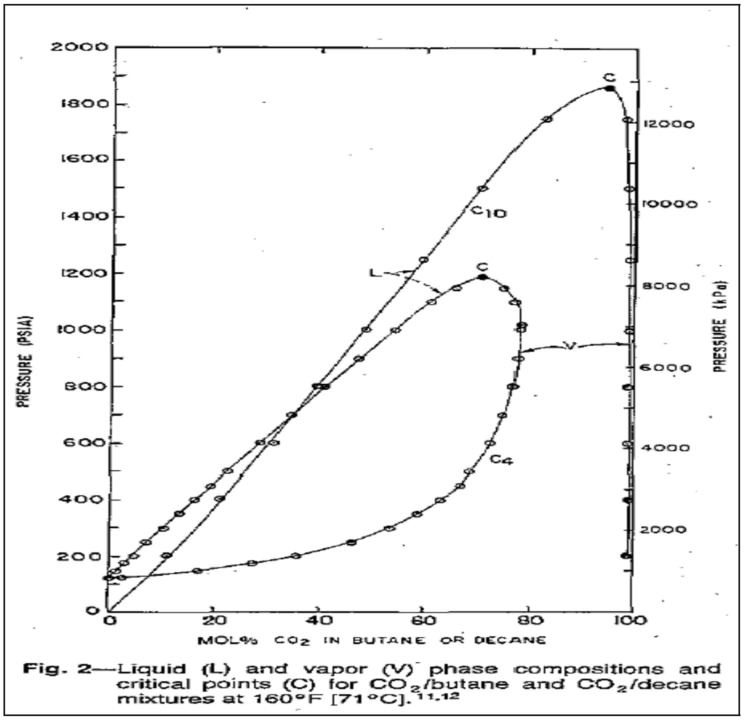


Figure 18: Pressure – Composition Diagram For CO_2 / n-Decane[56]

Benmekki and Mansoori[57] used pseudo-ternary diagrams for accurate visualization of miscibility for EOR purposes. They also tried to modify and use the Peng-Robinson (PR) EOS to accurately model the experimental P-X diagram of CO_2/n-Decane (at 160 ^oF). Although the modification is cumbersome to duplicate, the fit to the experimental data is good and predicts an MMP of 135 bars (1958 psi), which is in good agreement with the Orr and Jensen prediction.

4.2.2 From Commercial PVT Simulation Package

Due to non-availability of experimental facility or data at the desired temperature, the WINPROP® PVT package was used to predict the MMP between CO_2/n-Decane at 82 ^oF. However, the predictions of the simulator need be evaluated against compositional systems with known MMP values. To achieve this, two systems: one simple and other complex, with experimentally known values of MMP were used to calibrate the simulator. Then, this calibrated simulator was used to determine the MMP of CO_2/n-Decane (at 82 ^oF).

Simple system ($CO_2/C_4/C_{10}$)

Orr et al.[58] developed a rigorous tie line extension criterion for four components to determine MMP using a simple geometric construction. They cite Metcalfe and Yarborough (1970) as a base case for measurement of MMP. Metcalfe and Yarborough used a 60-40 mixture of n-Decane and butane to flood Berea sandstone cores, where they reported that the displacements at 1700 psia were Multiple Contact Miscible (MCM) and became First Contact Miscible (FCM) at 1900 psia. Because this is a simple system to test the effectiveness of MMP prediction for the WINPROP® PVT package, simulation runs were conducted for this mixture. The Peng – Robinson Equation Of State (PR EOS) predicted higher MMP values (~ 20% higher than experimental) for this system for both the MCM and FCM type of displacements. However, the Soave – Redlich – Kwong Equation Of State (SRK EOS) had a better prediction for this system. The WINPROP® PVT package predicted MMP values were in good agreement with the experimental values reported for the simple system.

Complex system (CO_2/Complex Stock Tank Oil (STO))

To further validate this technique of MMP determination, a complex STO mixture (C_7 to C_{28} fractions) was chosen from the literature[59], and its MMP was evaluated against pure CO_2. Excellent agreement with the correlation MMP and a fairly good match with experimental MMP values, as reported in the literature, were observed. The WINPROP® PVT package predicted MMP values were conservative compared to other methods, a trend also seen in the simple component system. Further, the SRK equation was found more to be agreeable to the experimental values, while maintaining its conservative nature.

Extension of results to the system of interest (CO_2/C_{10})

The encouraging results for known systems from the WINPROP® PVT package increased the confidence in the MMP prediction by this technique. To achieve maximum accuracy, the simple system ($CO_2/C_4/C_{10}$) was re-run and MMP predictions re-checked. The amount of C_4 in this mixture was decreased to 1.0%, 0.0000001% and finally 0.0%. The results expectantly show a steady increase in the MMP with the decrease in C_4 concentration. This is intuitive. Similar trends, as previously observed in simple and complex systems, regarding the MMP predictions were observed, and SRK gave a better fit than PR EOS.

A comparison between the experimental values of MMP and the calculated values from the simulations is shown in Table 3.

4.2.3 From empirical correlations

The other popular method for MMP determination is the empirical correlations. Ahmed(60) reviewed many of the popular empirical correlations used to determine MMP. Some of these empirical correlations were used to calculate the MMP of n-Decane with pure/impure CO_2 injection gas. The methods and the formulas used are summarized below.

Extrapolated Vapor Pressure (EVP) Method

This equation is called the Newittelal's equation, which states that, the EVP of any system is in good agreement with the MMP of the system. The equation is given below.

Table 3: Comparison between the experimental and calculated values of MMP.

Oil Composition	Inj. Gas	P-R Equation Of State		SRK Equation Of State		Experimental Values		Temp
		MCM	*FCM*	*MCM*	*FCM*	*MCM*	*FCM*	
60% C_{10} + 40% C_4	CO_2	1800 psia	2360 psia	1720 psia	2120 psia	1700 psia	1900 psia	160 ^oF
Complex STO (C_7 to C_{28})	CO_2	3160 psia	5000+ psia	3000 psia	5000+ psia	IFT Method: 2400 psig		50 ^oC
						Slim Tube: 2300 psig		50 ^oC
1% C_4 + 99% C_{10}	CO_2	3320 psia	3440 psia	2720 psia	2840 psia	--	--	160 ^oF
0.001% C_4 + 99.999% C_{10}	CO_2	1840 psia	3000+ psia	1760 psia	3000+ psia	--	--	82 ^oF
0.001% C_4 + 99.999% C_{10}	CO_2	3360 psia	3520 psia	2760 psia	2880 psia	--	--	160 ^oF
0.0% C_4 + 100.0% C_{10}	CO_2	3360 psia	3520 psia	2760 psia	2880 psia	Orr et al: 1800 psig		160 ^oF
						Benmekki: 1958 psig		160 ^oF

$$EVP = 14.7.EXP\left[10.91 - \frac{2015}{255.372 + 0.5556T}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where, Temperature (T) is in ^oF and EVP in psia

Petroleum Recovery Institute (PRI) Method

This method was developed by the Petroleum Recovery Institute (PRI), Canada. The correlation is included below.

$$MMP = 1071.82893 * 10^{(b)} \ldots\ldots\ldots\ldots b = \left[2.772 - (1519/T)\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Where, Temperature (T) is in ^oR and MMP in psia

Yellig and Metcalfe Method

Yellig and Metcalfe reported a simple equation to determine the MMP. However, the authors suggest that if the bubble point of the oil is greater than the predicted MMP, then the MMP be set equal to the bubble point pressure.

$$MMP = 1833.7217 + 2.2518055T + 0.01800674T^2 - 103949.93/T \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Where, Temperature (T) is in ^oF and MMP is in psia

Croqist Method

Croqist proposed another empirical correlation for determination of MMP of pure component systems. The correlation is included below.

$$MMP = 15.988T^{A} \ldots\ldots\ldots\ldots A = 0.744206 + 0.0011038M_{C5+} + 0.0015279Y_{CL} \ldots\ldots\ldots\ldots (7)$$

Where T is Reservoir temperature is in ^{o}F and Y_{CL} is Mole percentage of methane and nitrogen.

The MMP values for Newittelal's equation and Yellig and Metcalfe method were experimentally determined by Orr et al[(56)]. Currently, there are no reported experimental MMP verifications for the other two equations. However, the calculated values should not exceed +/- 12.5%, the error margin of the slim tube[(59)]. The results at 82 ^{o}F and 160 ^{o}F using these correlations are summarized in Table 4.

4.2.4 Discussion

The WINPROP® PVT package predicted MMP values are ***always*** conservative compared to any other method considered in this study. Furthermore, the SRK equation gave better results than PR equation for this system. Hence, we can safely use the MMP value predicted by WINPROP® using the SRK *without tuning* and assumed to be the miscible zone. Conducting the experiment at ~ 10% higher pressure than the highest predicted MMP value can help to guarantee development of miscibility.

4.3 Waterflood and Gas Displacement Results

The recovery and pressure drop data plots for all the Berea core-displacement tests conducted in this study are included in this section.

Table 4: Summary of all the MMP values obtained from empirical correlation calculations and comparison with available experimental values.

Empirical Correlation	82 ^oF	160 ^oF	Experimental (160 ^oF)
Newitteal	994.226	2309.6453	1880 psia
PRI	998.947	2249.7045	--
Yelling & Metcalfe	871.765	2005.2961	1880 psia
Croqist	814.961	1479.5276	--

4.3.1 1-ft Berea Core with 5% NaCl Brine Experiments

Figure 19 below shows the data obtained from 1-ft Berea core displacement tests with 5% NaCl brine solution as brine phase. This displacement test was conducted at 500 psi pressure where CO_2 is immiscible with n-Decane.

Part (a) provides the data for water recovery and pressure drop during the drainage cycle when n-Decane was injected into the brine saturated core.

Part (b) provides the data for oil recovery and pressure drop during the imbibition cycle when 5% NaCl brine was injected into the core at connate water saturation.

Part (c) provides the data for liquid and oil recoveries as well as pressure drop during the tertiary recovery process. The tertiary recovery process, in this case, is the continuous immiscible CO_2 gas injection.

Similar data for drainage, imbibition and tertiary gas injection for floods with 5% NaCl brine and 1-ft Berea cores are shown in figures 20 – 22. Part (c) of the figures presents the results for various modes of gas injection, viz. miscible versus immiscible, and continuous gas injection versus WAG injection. The results are discussed under section 4.4.

4.3.2 6-ft Berea Core with 5% NaCl Brine Experiments

Figure 23 below shows the data obtained from 6-ft Berea core displacement tests with 5% NaCl brine solution as brine phase. This displacement test was conducted at 500 psi pressure where CO_2 is immiscible with n-Decane.

Part (a) provides the data for water recovery and pressure drop during the drainage cycle when n-Decane was injected into the brine saturated core.

Part (b) provides the data for oil recovery and pressure drop during the imbibition cycle when 5% NaCl brine was injected into the core at connate water saturation.

Part (c) provides the data for liquid and oil recoveries as well as pressure drop during the tertiary recovery process. The tertiary recovery process, in this case, is the continuous immiscible CO_2 gas injection.

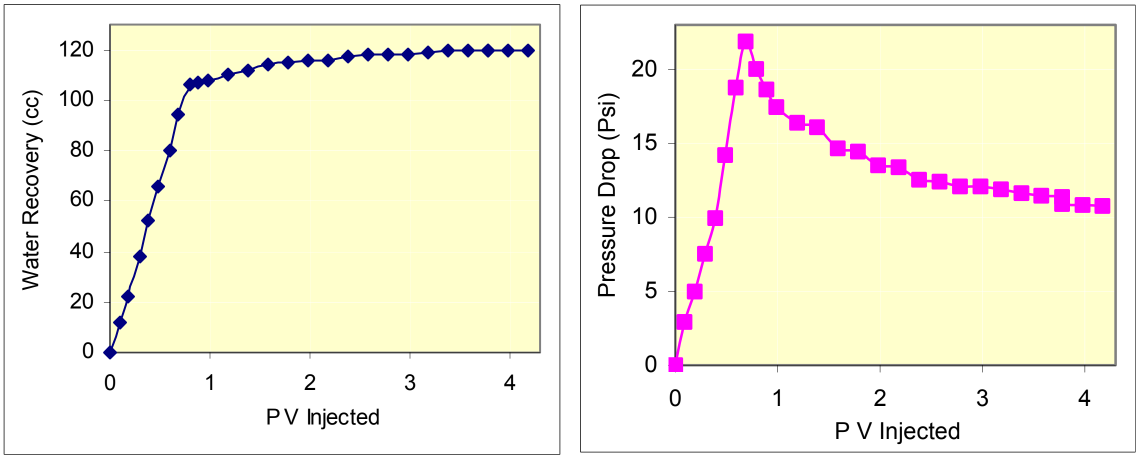
Similar data for drainage, imbibition and tertiary gas injection for floods with 5% NaCl brine and 1-ft Berea cores are shown in figure 24. Part (c) of the figures presents the results for various modes of gas injection, viz. continuous gas injection versus WAG injection. The results are discussed under section 4.4.

4.3.3 1-ft Berea Core with Yates Reservoir Brine Experiments

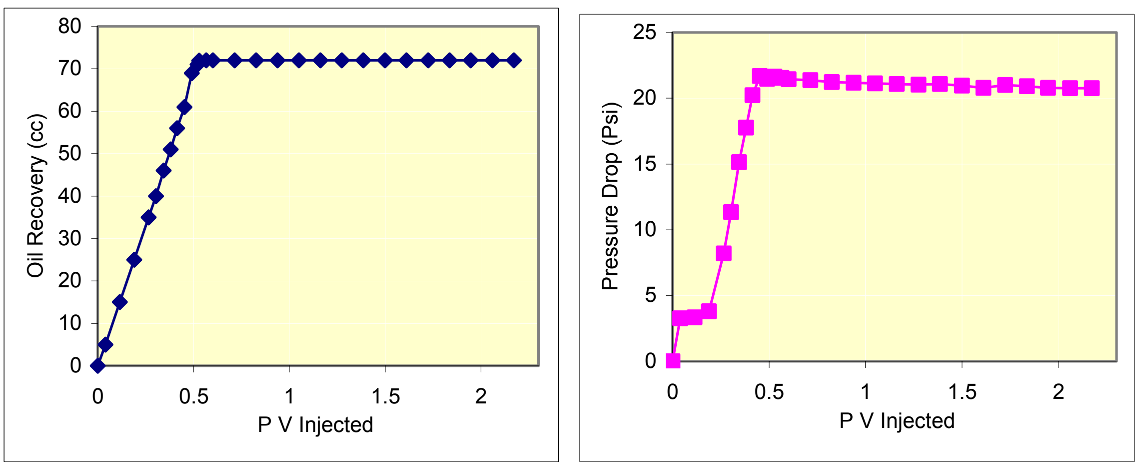
Figure 25 below shows the data obtained from 1-ft Berea core displacement tests with Yates reservoir synthetic brine solution as brine phase. This displacement test was conducted at 500 psi pressure where CO_2 is immiscible with n-Decane.

Part (a) provides the data for water recovery and pressure drop during the drainage cycle when n-Decane was injected into the brine saturated core.

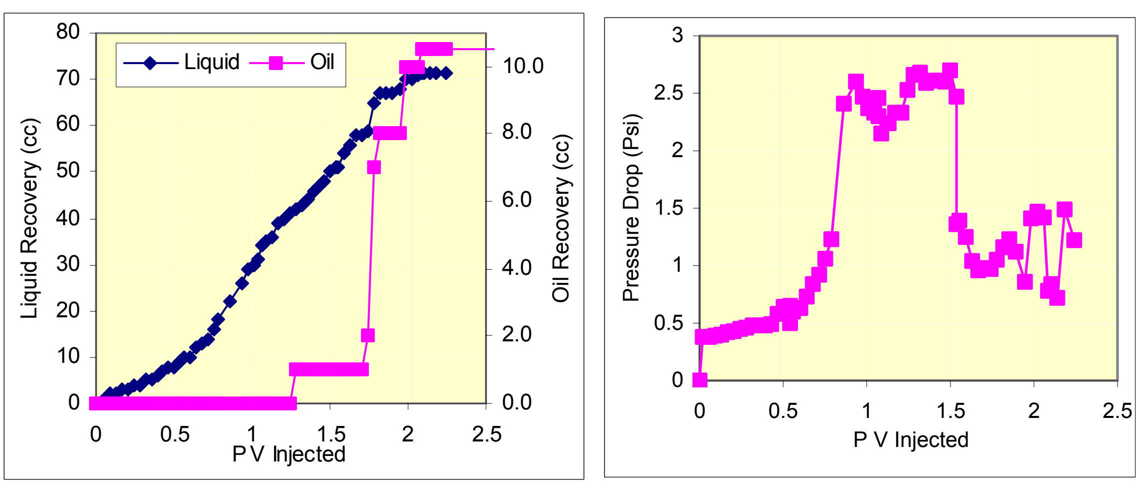
Part (b) provides the data for oil recovery and pressure drop during the imbibition cycle when Yates reservoir brine was injected into the core at connate water saturations.



(a) Drainage Cycle: Oil Flood with n-Decane.

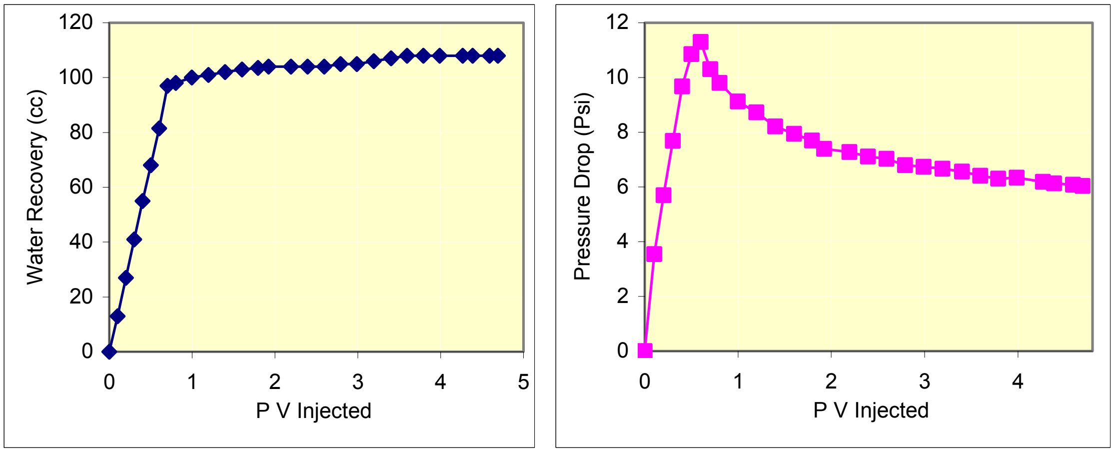


(b) Imbibition Cycle: Waterflood with 5 % NaCl Brine.

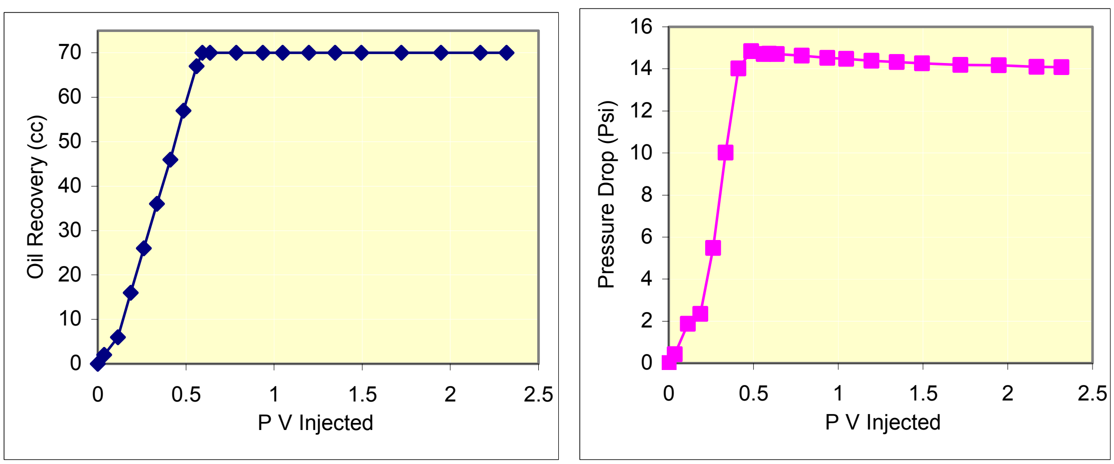


(c) Tertiary CO_2 Flood: Pure CO_2 continuous immiscible injection.

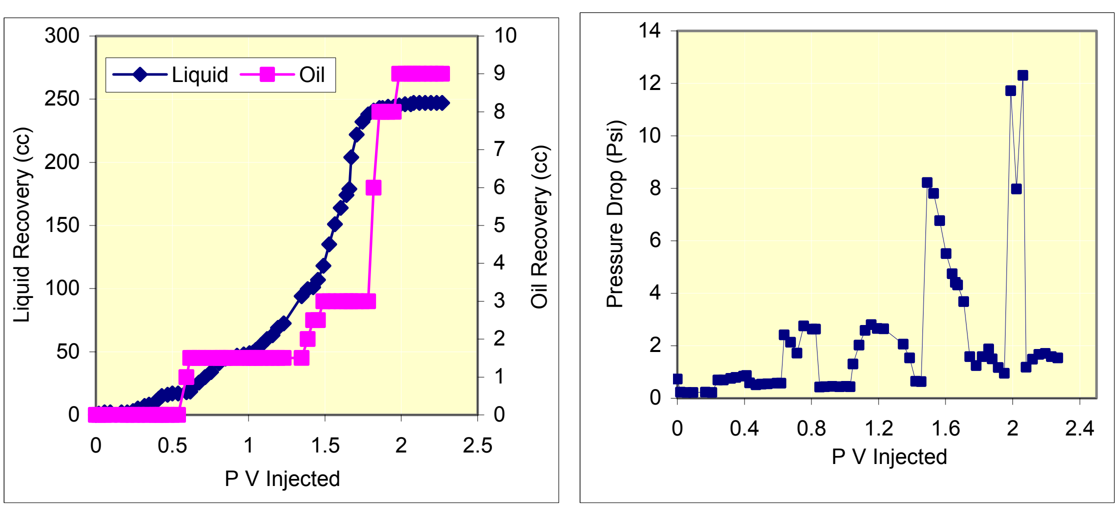
Figure 19: Data for experiment # 1: 1-ft Berea core + n-Decane + 5% NaCl brine with tertiary continuous CO_2 immiscible injection.



(a) Drainage Cycle: Oil Flood with n-Decane.

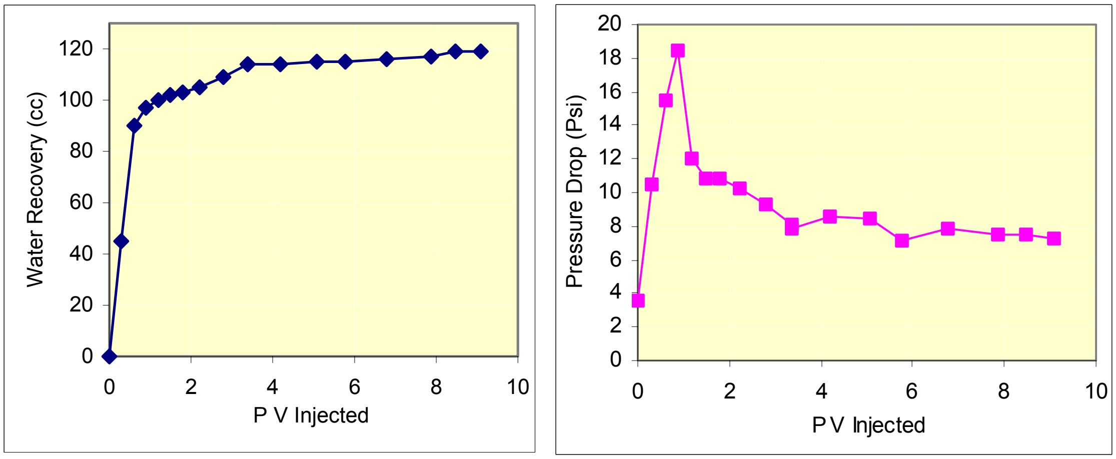


(b) Imbibition Cycle: Waterflood with 5 % NaCl Brine.

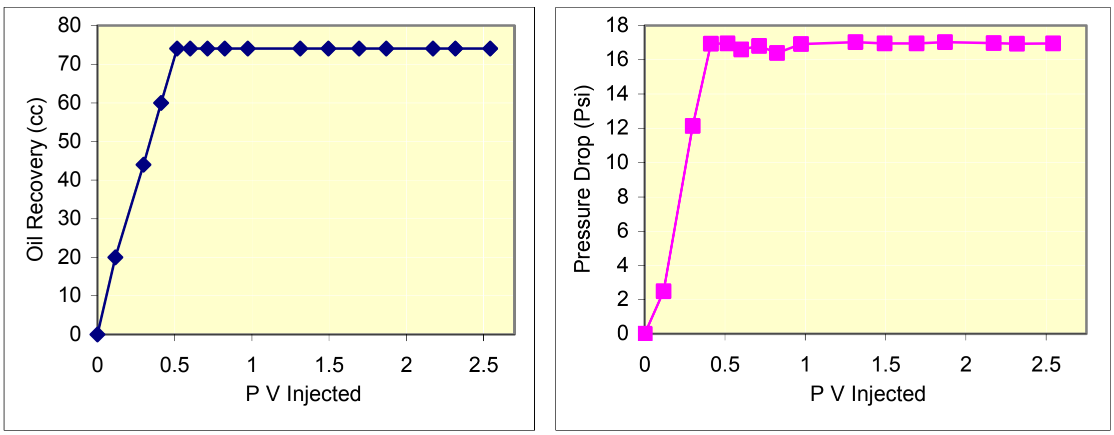


(c) Tertiary CO_2 Flood: Pure CO_2 alternating with water (WAG) immiscible injection.

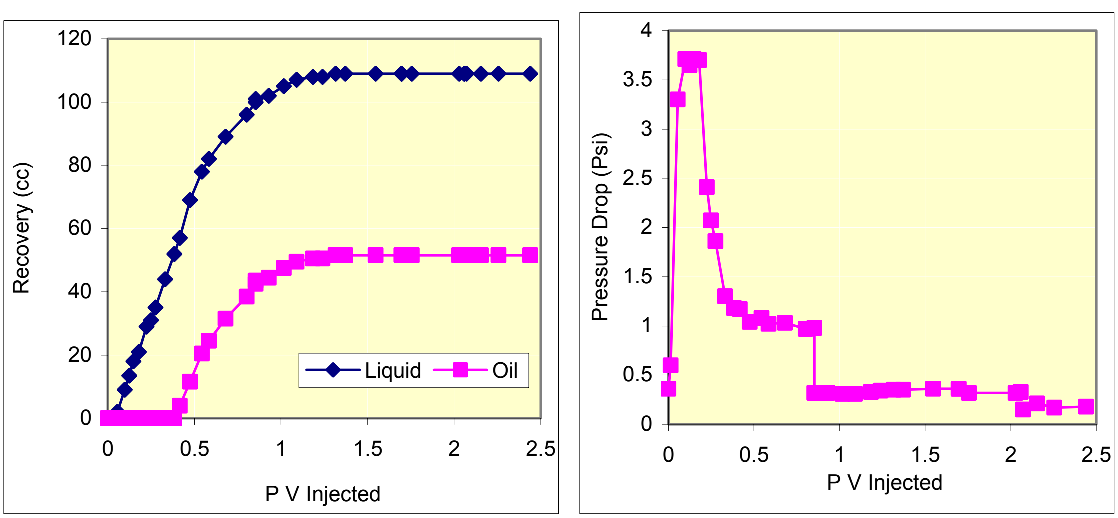
Figure 20: Data for experiment # 2: 1-ft Berea core + n-Decane + 5% NaCl brine with tertiary immiscible CO_2 WAG injection.



(a) Drainage Cycle: Oil Flood with n-Decane.

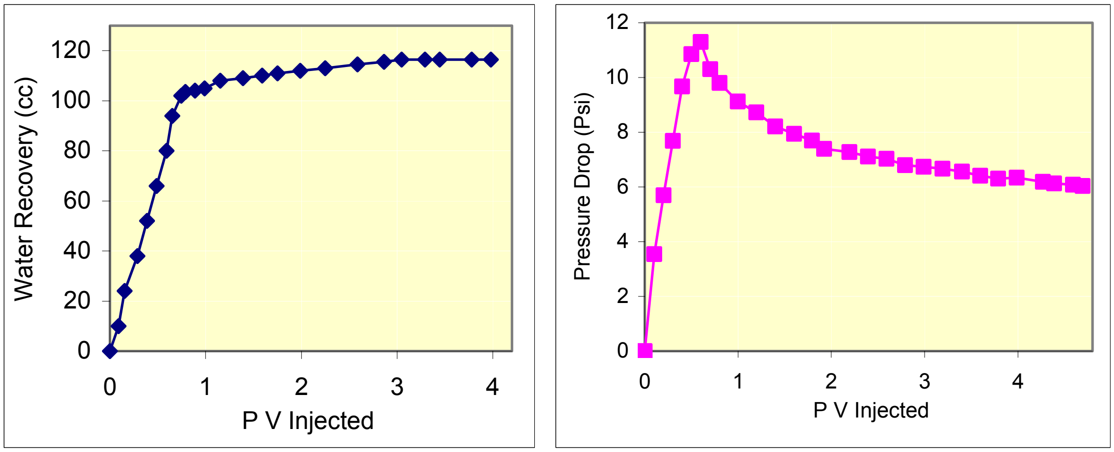


(b) Imbibition Cycle: Waterflood with 5 % NaCl Brine.

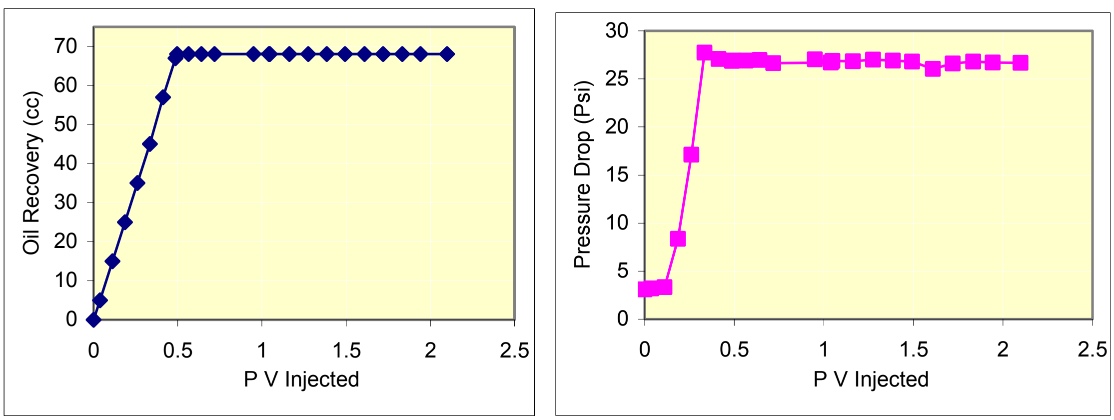


(c) Tertiary CO_2 Flood: Pure CO_2 continuous miscible injection.

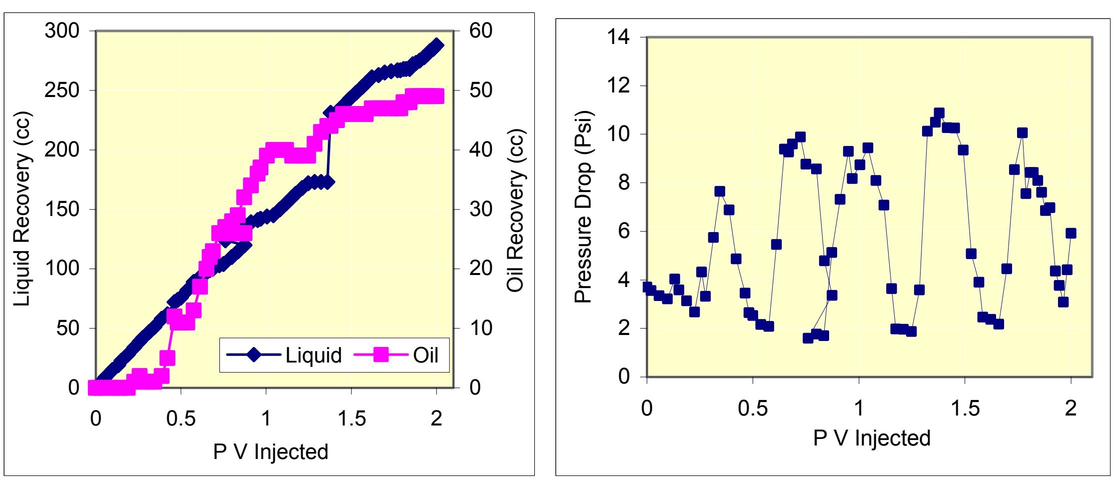
Figure 21: Data for experiment # 3: 1-ft Berea core + n-Decane + 5% NaCl brine with tertiary continuous CO_2 miscible injection.



(a) Drainage Cycle: Oil Flood with n-Decane.

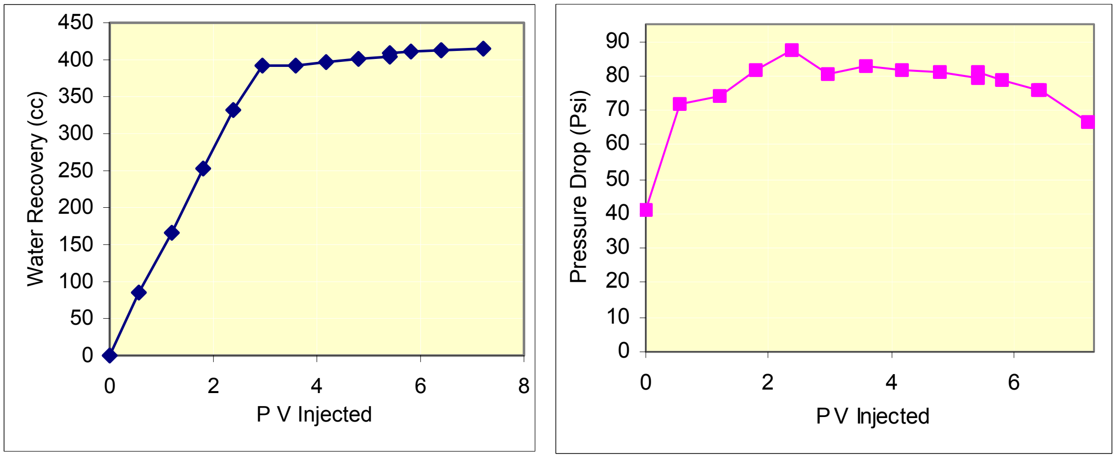


(b) Imbibition Cycle: Waterflood with 5 % NaCl Brine.

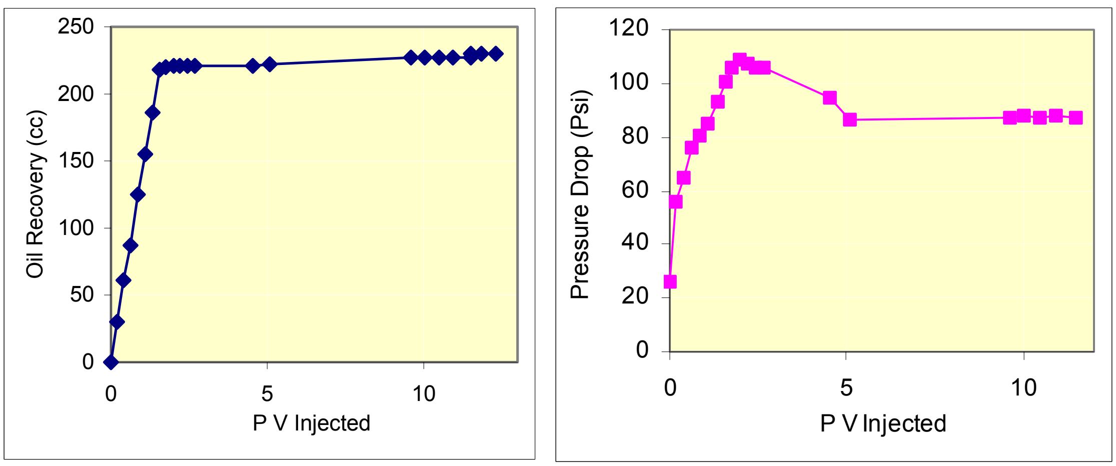


(c) Tertiary CO_2 Flood: Pure CO_2 alternating with water (WAG) miscible injection.

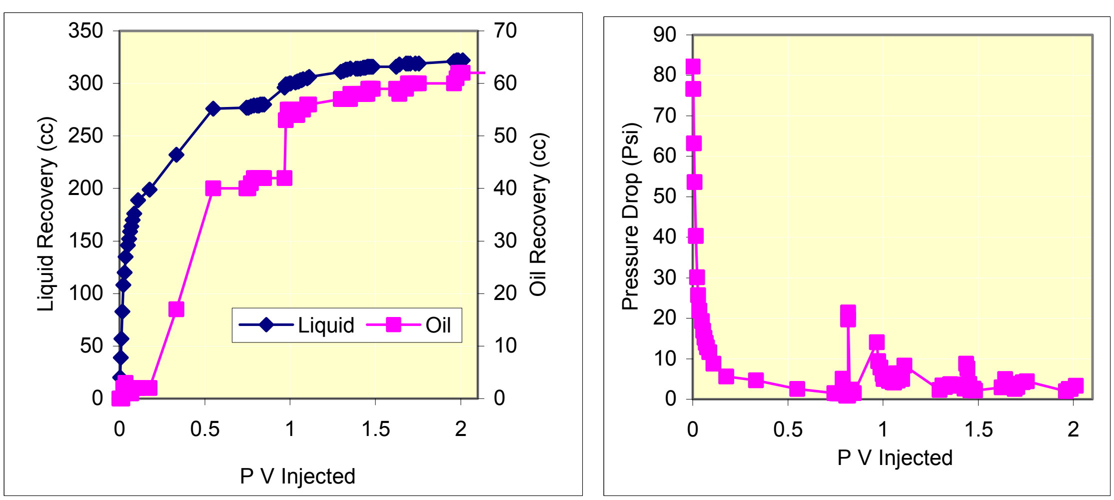
Figure 22: Data for experiment # 4: 1-ft Berea core + n-Decane + 5% NaCl brine with tertiary miscible CO_2 WAG injection.



(a) Drainage Cycle: Oil Flood with n-Decane

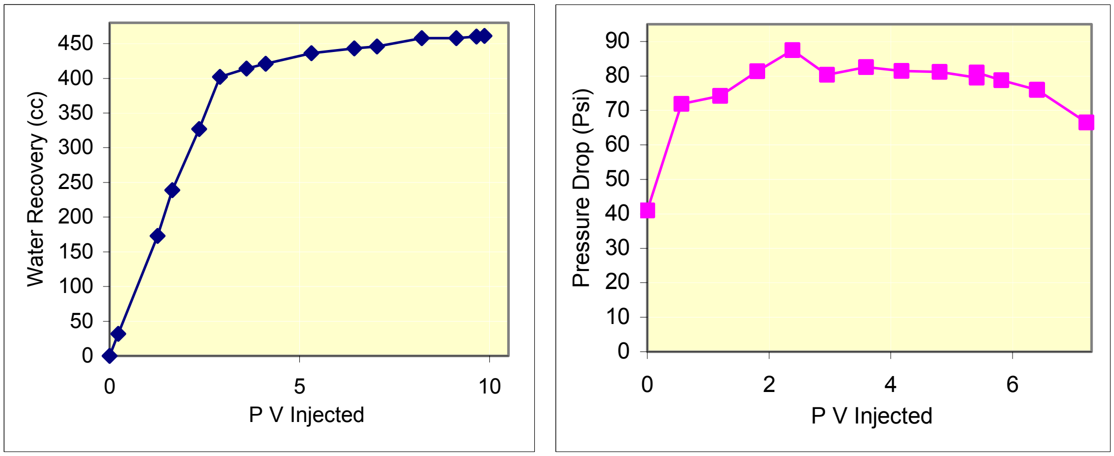


(b) Imbibition Cycle: Waterflood with 5 % NaCl Brine.

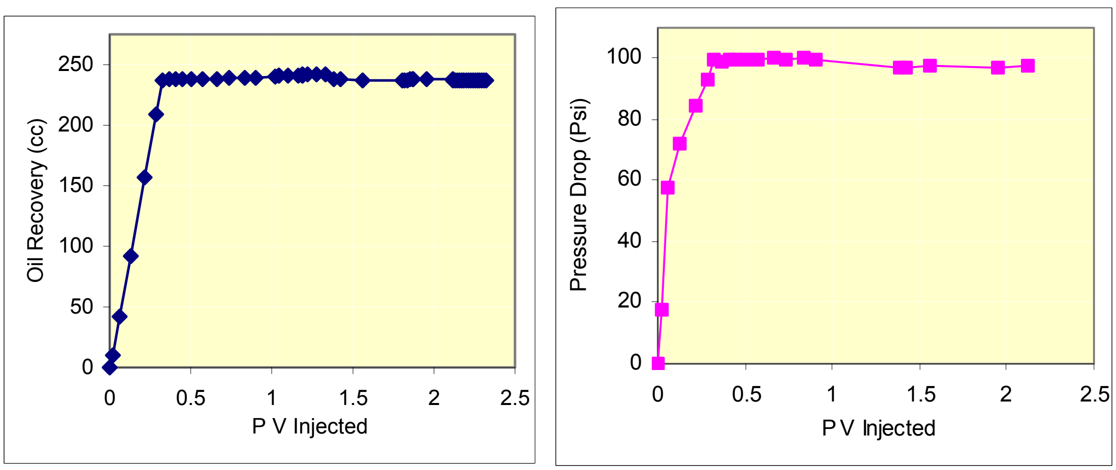


(c) Tertiary CO_2 Flood: Pure CO_2 continuous immiscible injection.

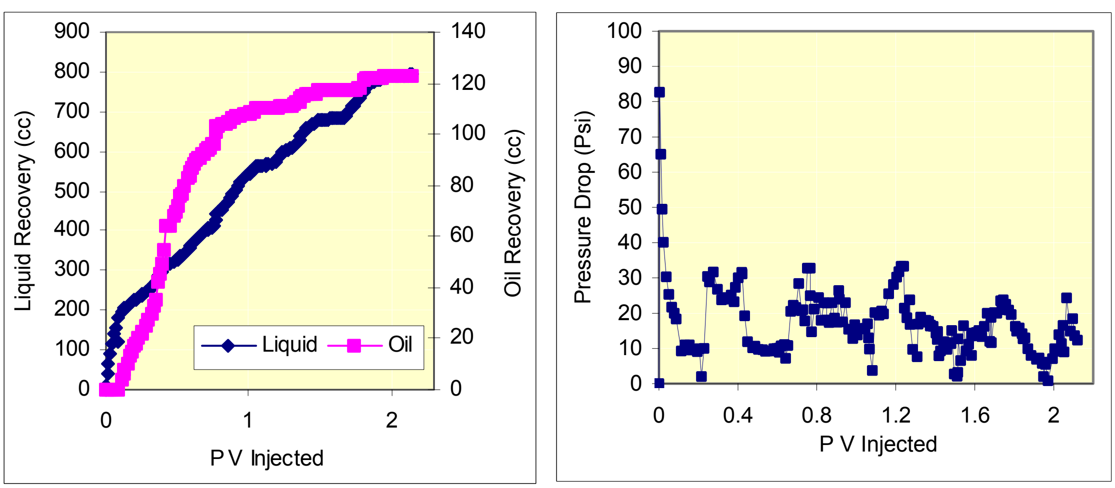
Figure 23: Data for experiment # 5: 6-ft Berea core + n-Decane + 5% NaCl brine with tertiary continuous immiscible CO_2 injection.



(a) Drainage Cycle: Oil Flood with n-Decane



(b) Imbibition Cycle: Waterflood with 5 % NaCl Brine.



(c) Tertiary CO_2 Flood: Pure CO_2 alternating with water (WAG) immiscible injection.

Figure 24: Data for experiment # 6: 6-ft Berea core + n-Decane + 5% NaCl brine with tertiary immiscible CO_2 WAG injection.

Part (c) provides the data for liquid and oil recoveries as well as pressure drop during the tertiary recovery process. The tertiary recovery process, in this case, is the continuous immiscible CO_2 gas injection.

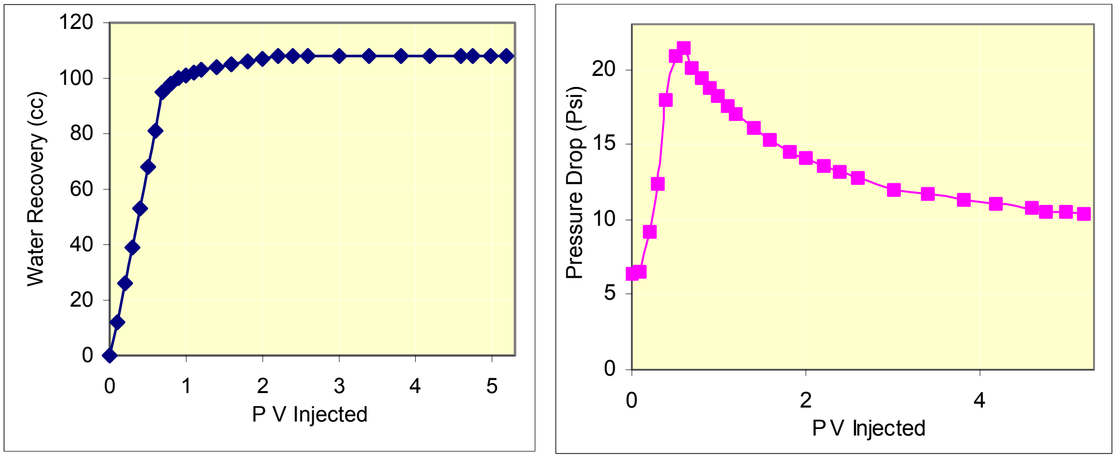
Similar data for drainage, imbibition and tertiary gas injection for floods with Yates reservoir brine and 1-ft Berea cores are shown in figures 26 - 28. Part (c) of the figures present the results for various modes of gas injection, viz. immiscible versus miscible, and continuous gas injection versus WAG injection. The results are discussed under section 4.4.

4.4 Results from Core Tests

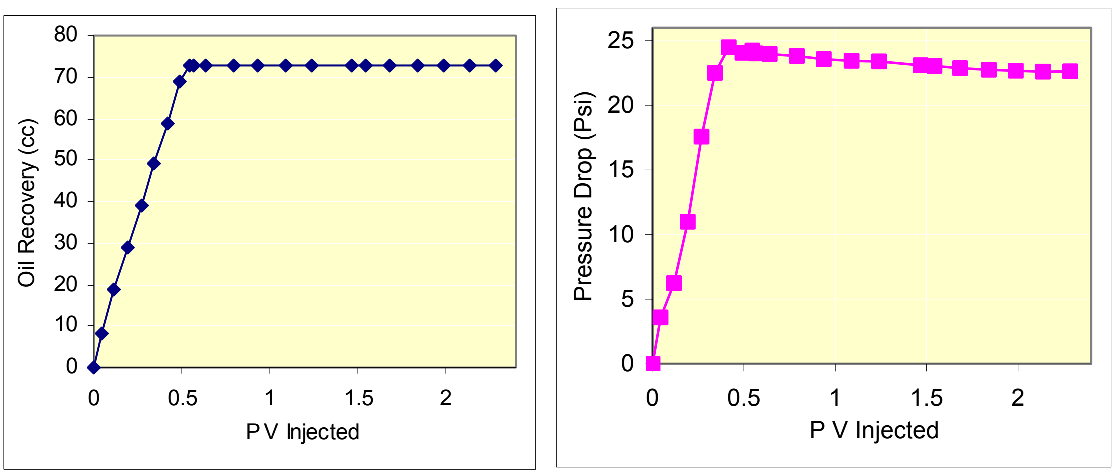
The core tests were conducted in three steps. The preliminary oil flood was used to measure the connate water saturation of the core. Brine was injected into the core to determine the secondary recovery and residual oil saturation to a waterflood. Tertiary gas injection (Continuous gas injection or WAG injection) followed the secondary flood to evaluate the efficiency of this procedure. The results of the core tests conducted in this work are discussed below:

The objective of the tests was to determine the effects of mode of tertiary gas injection (CGI or 1:1 WAG), miscibility, brine composition and core length, on dynamic displacement tests in Berea cores.

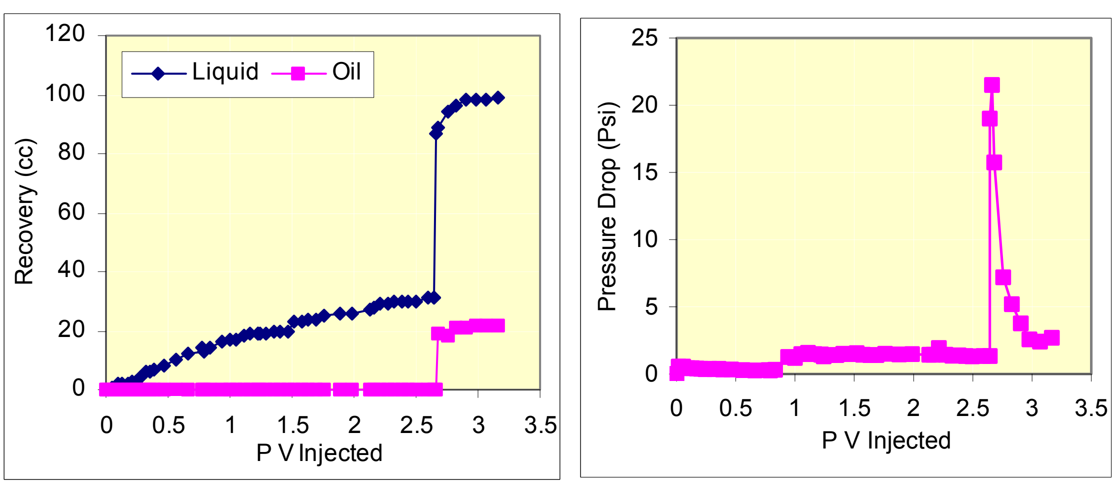
These tests were conducted at 500 psi (immiscible) and 2500 psi (miscible). Two types of brines (viz. 5% NaCl and Yates) were used and tertiary CO_2 floods were conducted in two modes (viz. Continuous Gas Injection (CGI) and WAG). The tests with 5% NaCl brine were conducted on both, 1-ft and 6-ft Berea cores to determine the effect of core length on dynamic displacements.



(a) Drainage Cycle: Oil Flood with n-Decane.

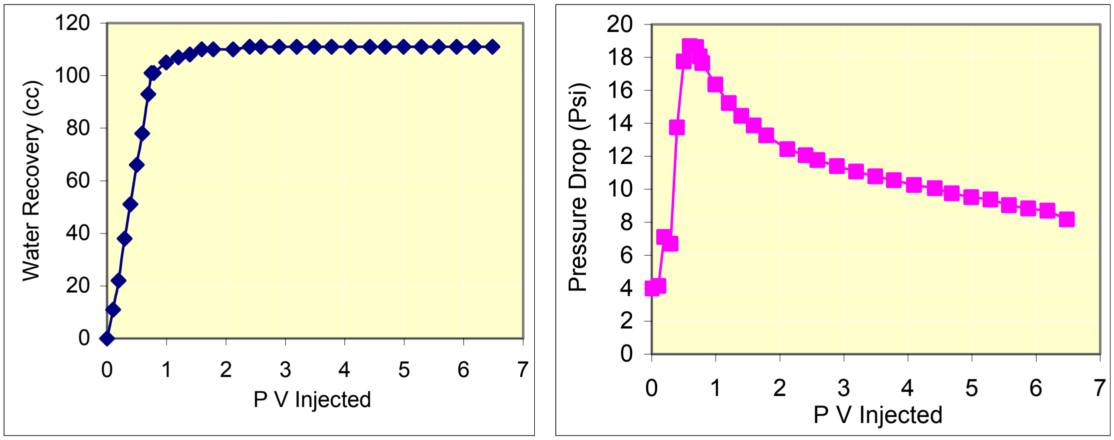


(b) Imbibition Cycle: Waterflood with Yates synthetic Brine.

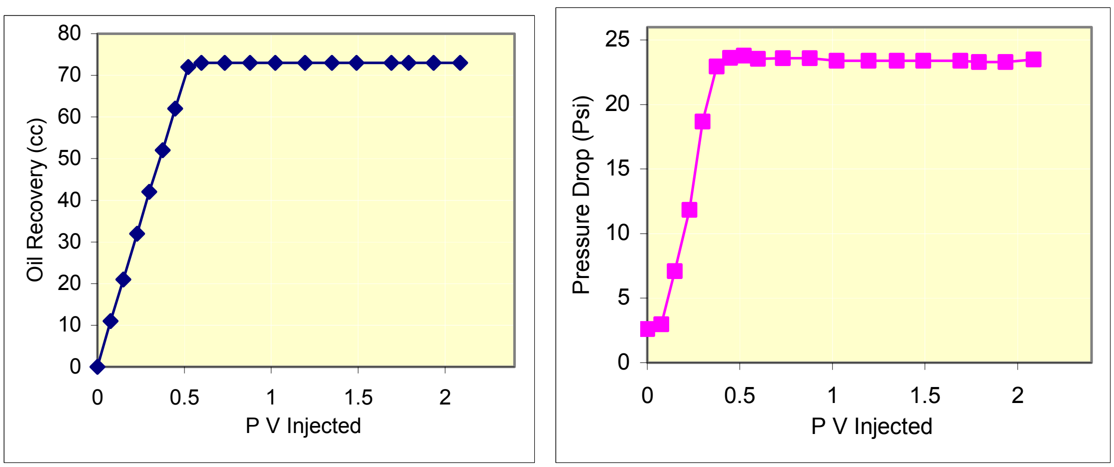


(c) Tertiary CO_2 Flood: Pure CO_2 continuous immiscible injection.

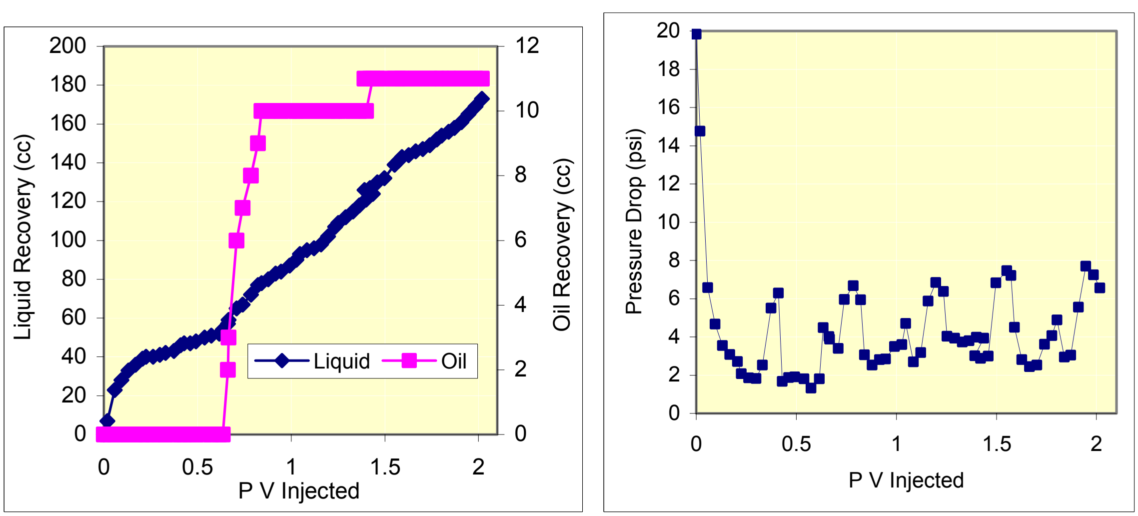
Figure 25: Data for experiment # 7: 1-ft Berea core + n-Decane + Yates synthetic brine with tertiary continuous CO_2 immiscible injection.



(a) Drainage Cycle: Oil Flood with n-Decane.

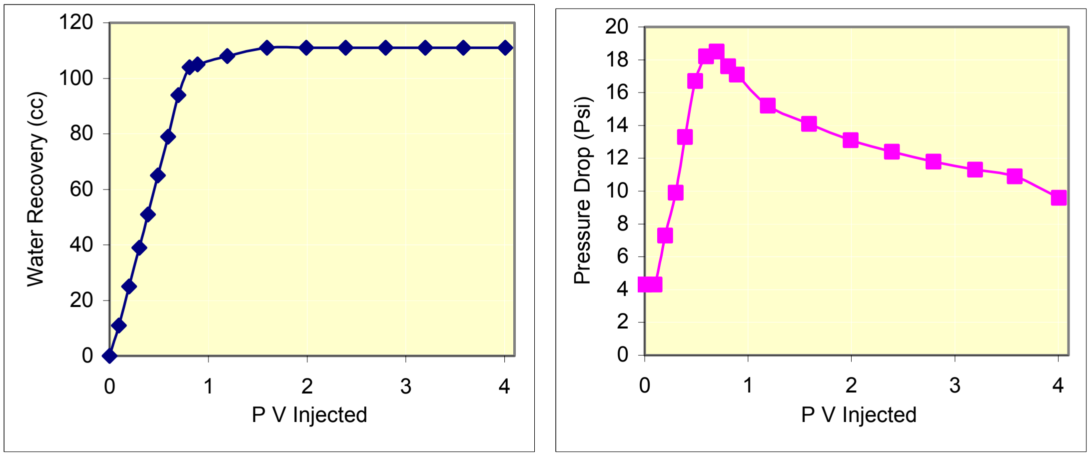


(b) Imbibition Cycle: Waterflood with Yates synthetic Brine.

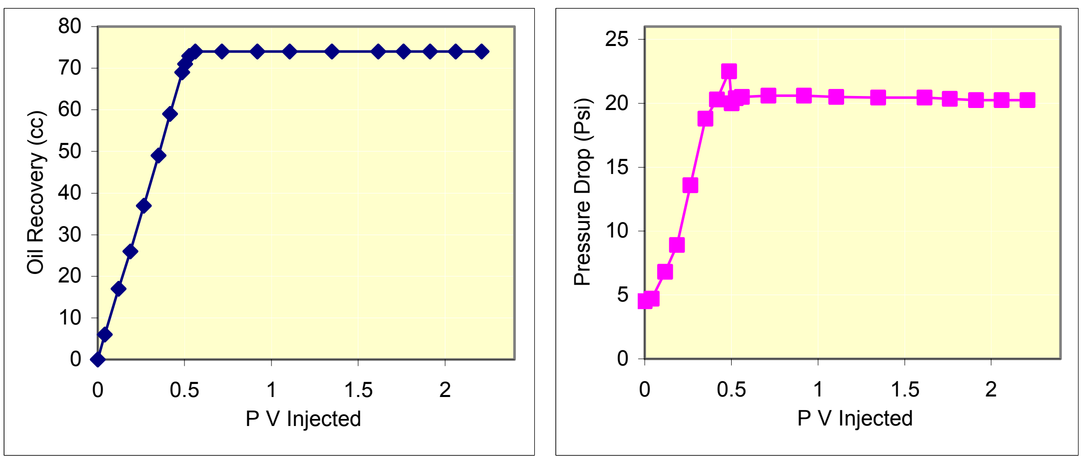


(c) Tertiary CO_2 Flood: Pure CO_2 alternating with water (WAG) immiscible injection.

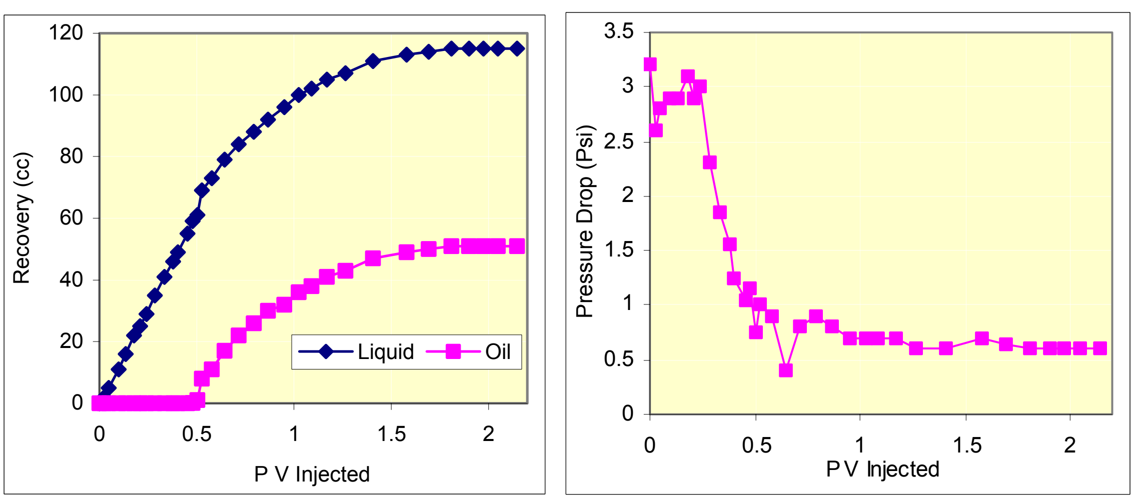
Figure 26: Data for experiment # 8: 1-ft Berea core + n-Decane + Yates synthetic brine with tertiary immiscible CO_2 WAG injection.



(a) Drainage Cycle: Oil Flood with n-Decane

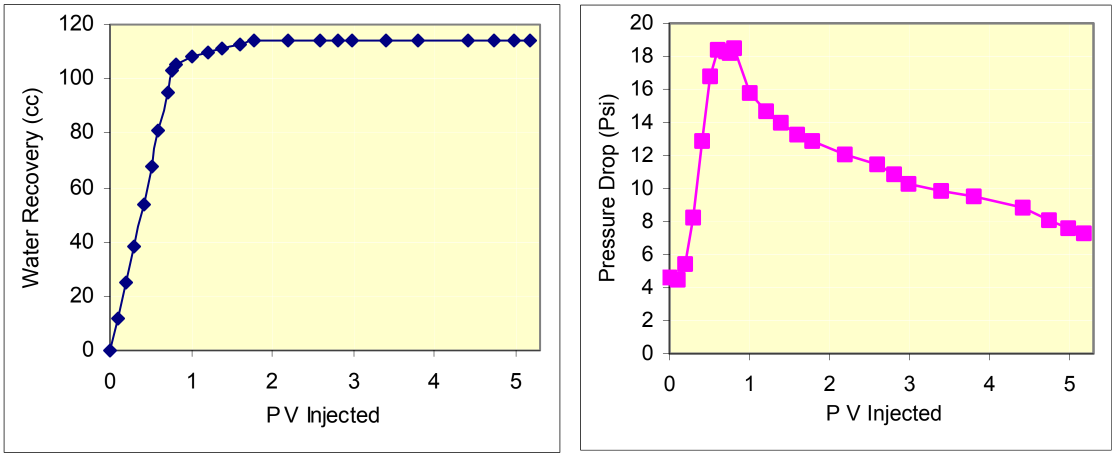


(b) Imbibition Cycle: Waterflood with Yates synthetic Brine.

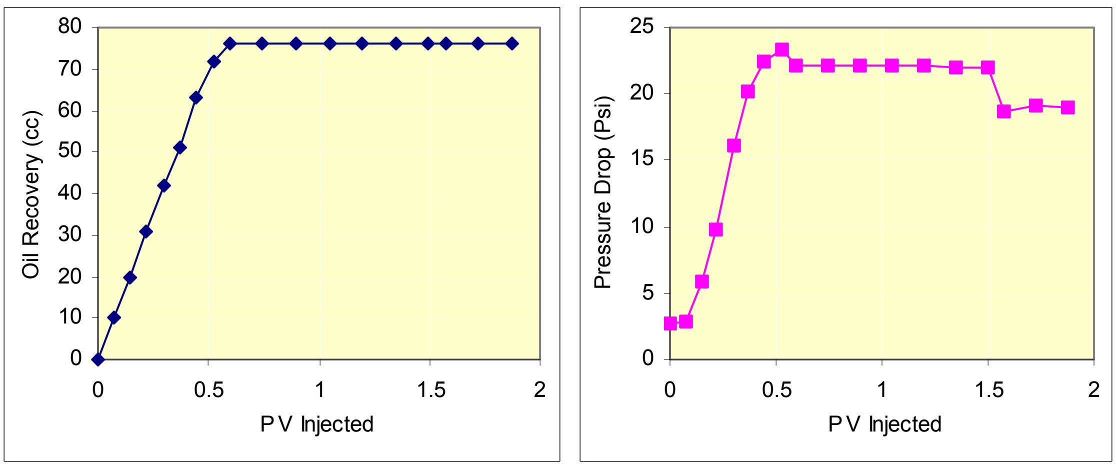


(c) Tertiary CO_2 Flood: Pure CO_2 continuous miscible injection.

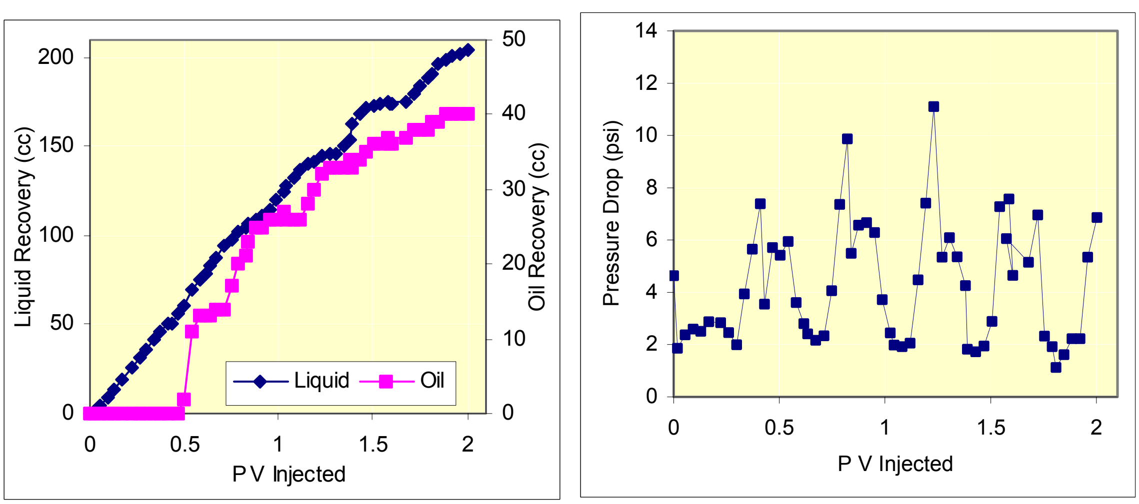
Figure 27: Data for experiment # 9: 1-ft Berea core + n-Decane + Yates synthetic brine with tertiary continuous CO_2 miscible injection.



(a) Drainage Cycle: Oil Flood with n-Decane



(b) Imbibition Cycle: Waterflood with Yates synthetic Brine.



(c) Tertiary CO_2 Flood: Pure CO_2 alternating with water (WAG) miscible injection.

Figure 28: Data for experiment # 10: 1-ft Berea core + n-Decane + Yates synthetic brine with tertiary miscible CO_2 WAG injection.

The Berea sandstone cores used for the test were fresh, without any previous history of exposure to crude oil. This is important because exposure to crude oils could have wettability effects rendering erroneous measurements and non-representative displacement characteristics. In order to eliminate the effects of rock heterogeneity, all the core tests were conducted on the same 1-ft Berea sandstone core using a non-reactive n-Decane as the oil phase and adopting a through cleaning procedure in between the various displacements.

4.4.1 Oil Flood

This cycle constitutes the process of injection of n-Decane into the core that is initially saturated with brine to get connate water saturation. This is an important step that determines the original oil in place (OOIP). The relative permeability of the core to oil at the end of this cycle is an important wettability identification parameter. The Craig's rules of thumb(53) were used to infer wettability from relative permeability end points.

5 % NaCl Brine + n-Decane + Berea Core

The results for this system are given in Table 5. As can be seen in Table 5, high oil saturations consequently lower connate water saturations were characteristic of the 1-ft Berea core system. However, 6-ft cores show higher connate water saturations when 2.0 PV of oil were flooded through. This suggests higher pore-volume injection requirements for the 6-ft system. Especially low relative oil permeabilities at the end of the oil flood were observed in all the cases.

Berea sandstone cores are known to be strongly water-wet in nature. The low end point oil relative permeabilities and lower connate water saturations indicate intermediate to oil-wet characteristics as suggested by Craig's rules of thumb. The larger variations in the absolute permeability values, compared to the other system (Yates brine with n-

Decane in a Berea core), suggest the unstable nature of the system, in spite of the consistent and rigorous cleaning procedure practiced.

Berea cores are known to be highly sensitive and show wide variations in the displacement characteristics if the clays are not stabilized. Literature[(41)(42)(44)(45)] suggests the use of brines containing divalent cations such as $[Ca^{++}]$ and $[Mg^{++}]$ and firing of the core to stabilize the clays in Berea sandstone. Experimental evidences have shown the process to be reversible[(62)] and the ions attached to clay surfaces easily interchanged by flowing a solution of another salt through the core. Hence, another series of experiments using the same core but with Yates reservoir brine, containing divalent cations, was designed to investigate this phenomenon.

Yates reservoir Brine with n-Decane in Berea Core

The monovalent brine used in the previous experiments was replaced with a multivalent (Yates reservoir) brine to investigate the phenomena of clay stabilization and its effects on dynamic displacement corefloods.

Since the corefloods were conducted on the same core, the cleanup was done using the 5% brine initially and then this brine was miscibly displaced by Yates reservoir multivalent brine. This was done to ensure that the core was subjected to the same history as the other tests. To stabilize the clays in the core, 24 hours of ageing with multivalent brine after each cleanup was done. The 24-hour ageing period was found to be optimum from contact angle studies at LSU Rock-Fluid Interactions Laboratory[(61)]. The S_{WC}, connate water saturations and the end-point oil relative permeabilities for the corefloods conducted are summarized in the Table 5 below.

The oil cycles conducted with multivalent brine (experiment # 7 – 10) showed significant increase in the end point oil permeabilities as well as the connate water saturations compared to those with 5% NaCl brine. Similar experiments conducted on Berea core by Thomas / Archer showed comparable oil saturations with these cycles after the oil flood. A significant reduction in the standard deviation of the absolute permeability indicates that stabilization of the core clays and shift of the system from intermediate to oil-wet (5% NaCl brine runs) to more water-wet characteristics has occured.

Table 5: Summary of Oil Flood (Drainage) Cycles

Expt No.	Experiment Title	P_{TEST} (psi)	Abs. Perm (D)	S_{WC}	S_{OI}	End Point Rel-Perms
5 % NaCl Brine + n-Decane + Berea Core						
1	1-ft Immiscible Continuous CO_2	500	0.2526	12.5	87.5	34.5 %
2	1-ft Immiscible CO_2 WAG	500	0.3435	21.3	78.7	39.9 %
3	1-ft Miscible Continuous CO_2	2500	0.2895	13.3	86.7	42.0 %
4	1-ft Miscible CO_2 WAG	2500	0.1825	15.1	84.9	47.0 %
5	6-ft Immiscible Continuous CO_2	500	0.1844	44.7	55.3	44.2 %
6	6-ft Immiscible CO_2 WAG	500	0.2463	38.5	61.5	33.7 %
Yates synthetic Brine + n-Decane + Berea Core						
7	1-ft Immiscible Continuous CO_2	500	0.1311	21.3	78.7	65.5 %
8	1-ft Immiscible CO_2 WAG	500	0.1869	19.1	80.9	58.3 %
9	1-ft Miscible Continuous CO_2	2500	0.1443	18.4	81.6	59.1 %
10	1-ft Miscible CO_2 WAG	2500	0.1906	16.9	83.1	66.8 %

4.4.2 Brine Floods

This cycle constitutes the process of brine injection into the core, which is at connate water saturation, to get water-flood residual oil saturation in the core. Brine is injected at stable flow rates into the core after the drainage cycle. This step is an indicator of the extent of feasible secondary oil recovery. The end point permeability of the rock to brine at the end of this cycle can also be used to infer wettability. The recovery of residual oil saturations and end point water relative permeabilities for the waterflood conducted are summarized in the Table 6.

The imbibition results are typical of water-wet cases for both the brine systems (namely 5% NaCl brine and Yates reservoir brine) used for these tests. Excellent agreements of recoveries between all the imbibition (1-ft and 6-ft Berea core) displacements were found. Higher waterflooding recoveries, low end point water permeabilities, a sharp breakthrough with negligible oil production after breakthrough (seen in the plot of oil recovery vs. PV Injected), all the characteristics of a water-wet rock, were exhibited in the cycle.

Table 6: Summary of Brine Flood (Imbibition) Cycles

Expt No.	Experiment Title	P_{TEST} (psi)	S_{OR}	S_W	Recovery % OOIP	End Pt Rel-Perms
5 % NaCl Brine + n-Decane + Berea Core						
1	1-ft Immiscible Continuous CO_2	500	35.0	65.0	60.0 %	08.01 %
2	1-ft Immiscible CO_2 WAG	500	27.7	72.3	64.8 %	08.09 %
3	1-ft Miscible Continuous CO_2	2500	32.8	67.2	62.2 %	08.05 %
4	1-ft Miscible CO_2 WAG	2500	35.4	64.7	58.4 %	08.72 %
5	6-ft Immiscible Continuous CO_2	500	24.7	75.3	55.4 %	17.60 %
6	6-ft Immiscible CO_2 WAG	500	23.7	76.3	61.4 %	10.03 %
Yates synthetic Brine + n-Decane + Berea Core						
7	1-ft Immiscible Continuous CO_2	500	25.5	74.5	67.6 %	11.80 %
8	1-ft Immiscible CO_2 WAG	500	27.7	72.3	65.8 %	07.51 %
9	1-ft Miscible Continuous CO_2	2500	29.9	70.1	66.7 %	11.56 %
10	1-ft Miscible CO_2 WAG	2500	27.0	73.0	66.7 %	09.39 %

4.4.3 Tertiary Gas Injection Floods

Two types of experiments were conducted: Continuous Gas Injection (CGI) and Water-Alternating-Gas (WAG). Gas injection is a popular EOR process in light oil reservoirs. As the literature review suggests, almost 80% of the gas injection processes employ the WAG method. The continuous CO_2 injection process and 1:1 WAG (with 0.2 PV slug size) are the most popular gas injection EOR processes employed in the field today. Hence, investigation of the displacement characteristics for these tertiary processes was conducted.

The main objectives of this portion of the project are to determine the effects of miscibility, brine composition and core length. These effects are illustrated below after defining two parameters that enable valid comparisons of various experiments.

The evaluation of all the corefloods conducted at various conditions and tertiary recovery modes, requires a common parameter for comparison. Two new factors were defined, 'CO_2 utilization factor (UF_{CO2})' and 'Tertiary Recovery Factor (TRF)' as the Fraction of residual oil in place recovered per pore volume of CO_2 injected (ROIP/PV-CO_2). These are used to compare the relative merits of all the corefloods conducted, and are defined below:

CO_2 utilization factor (UF_{CO2}) is commonly used to evaluate field projects and is defined as the volume of CO_2 gas injected under standard conditions, to produce a barrel of oil, and is calculated as:

$$UF_{CO2} = \frac{V_{CO2}(MSCF)}{Q_{Oil}(Bbl)} \quad \text{...(8)}$$

Fraction of Residual oil In Place (ROIP) recovered per Pore Volume (PV) of CO_2 injected (ROIP/PV-CO_2): The corefloods conducted were in CGI and WAG mode, which resulted in an unequal quantities of cumulative gas injection for each flood. To 'normalize' the recoveries and avoid fallacious conclusions from the data, the ROIP/PV-CO_2 factor was defined as below,

Dimensionless TRF = [(Oil recovered cc)/(S_{OR} cc)]/[Cum. PV CO2 Injected]…………....(9)

This factor has been calculated for each experimental data point. The use of these two factors in the analysis was found to be more appropriate as shown in the flowing comparisons. However, the standard plots, such as recovery vs. PVI are also included for easy cross-reference.

All the results of the tertiary gas injection floods are summarized in Section 4.4 below and individual objectives namely effect of miscibility, brine composition and core length are discussed.

4.5 Discussion of Tertiary Gas Injection Floods

4.5.1 Effect of Miscibility

Miscibility affects the microscopic displacement efficiency in the gas injection EOR process. It influences the capillary number through interfacial tension. A zero interfacial tension value is necessary and sufficient for attainment of miscibility. Hence, miscible floods have relatively high capillary numbers that result in increased oil recovery.

Miscible and immiscible floods were conducted using the two sets of fluid systems, namely 5% NaCl brine with n-Decane and Yates reservoir brine with n-Decane on 1-ft Berea core. The individual plots are included below as Figures 29 – 30 respectively.

5 % NaCl Brine + n-Decane + 1-ft Berea Core System

Both WAG and continuous mode gas injection floods were conducted using 5% NaCl brine + n-Decane + 1-ft Berea core. The results are included in Figure 29 below.

As suggested earlier, this increase is attributable to the significant reductions in interfacial tension between the displacing and displaced fluids by virtue of miscibility development. This results in very high capillary numbers and consequently near perfect microscopic displacement efficiency. Hence, the development of miscibility is beneficial from a recovery point of view.

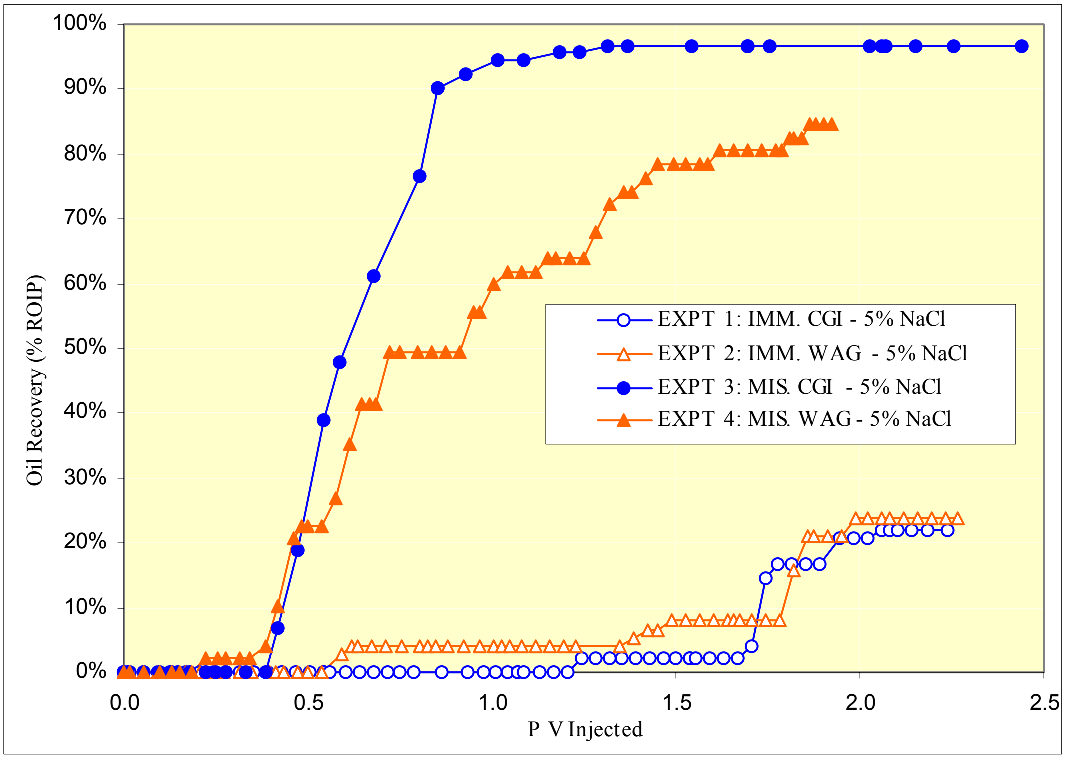


Figure 29 (a): Recovery in % of ROIP

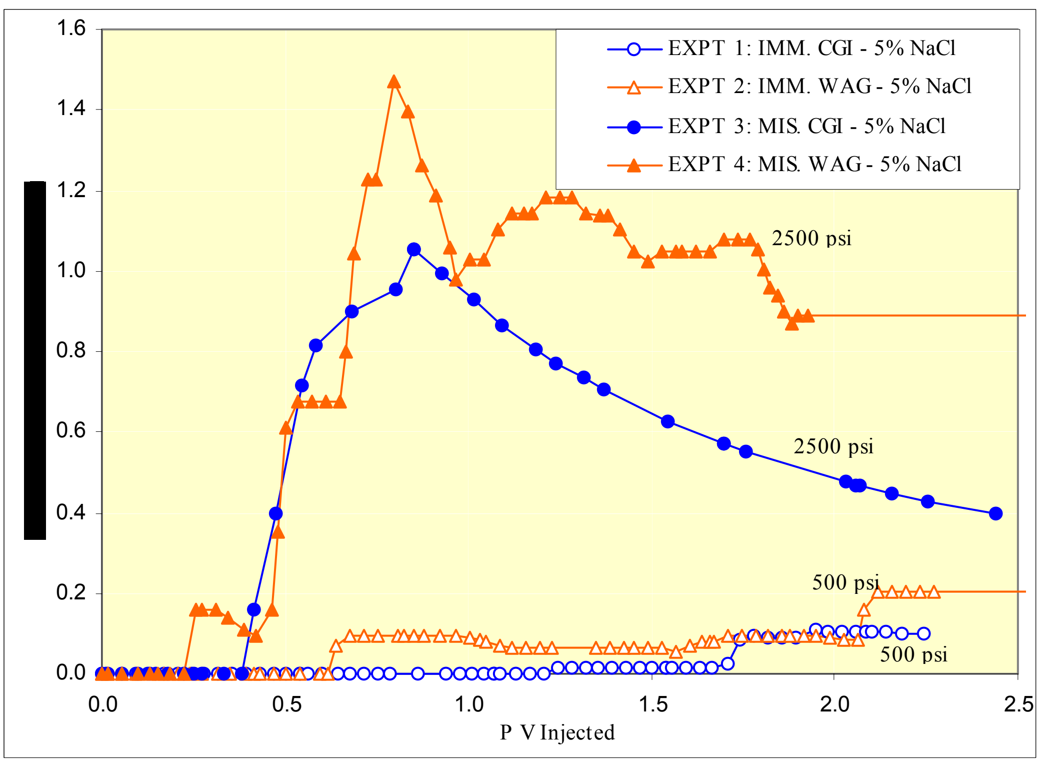


Figure 29 (b): Recovery As Fraction of Residual Oil In Place Per PV of CO_2 Injected
Figure 29: Effect of Miscibility and Mode of Injection in Tertiary Recovery in 5% NaCl Brine + n-Decane

Figure 29(a) also appears to indicate that there is minimal advantage to using the WAG in immiscible mode. Further, miscible CGI is desirable from the recovery point of view. These conclusions are misleading because, the amount of CO_2 injected for these recoveries are significantly different for each floods. The total recovery obtained from 1:1 WAG is from half the volume of CO_2 gas injected for the CGI process. Hence, the analysis of the results on the basis of recovery only leads to erroneous comparisons. It is for this reason the recoveries were 'normalized' on the basis of waterflood residual oil recovered per pore volume (PV) of CO_2 gas injected to arrive at the Tertiary Recovery Factor defined earlier. This factor is plotted in Figure 29(b).

Figure 29 indicates significant increase in oil recovery in miscible floods, while the recoveries in immiscible floods (both CGI and WAG) were about 23%, the miscible floods yielded 93.7% recovery for the CGI floods and 84.5% for the WAG flood. This further indicates that in these 1-ft Berea core floods, the continuous injection of CO_2 appears to have performed better than WAG injection. However, it should be noted the CGI floods utilize twice the volume of CO_2 to that of WAG floods. Hence, a valid comparison of the two would be on the basis of TRF that normalizes the recovery with respect to the CO_2 volumes injected. This is the purpose of Figure 29(b).

The Figure 29(b) clearly shows the advantage of the WAG process. Both, miscible and immiscible processes hasten recovery and result in better process economics. It is important to note the conclusions from Figures 29(a) and 29(b) are contradictory. Thereby, the use of ROIP/PV-CO_2 factor for evaluation of the corefloods is appropriate and is used in analyzing the rest of the experimental results (along with the conventional recovery plots).

It is interesting to note that, in Figure 29(b), the TRF for experiment 3 for the CGI miscible flood continuously decreases and approaches the data for immiscible floods. This has serious implications such that appeared to be the best case scenario based on the recovery plot, but turns out to the worst case due to the cost of compressing CO_2 to pressures above the minimum miscibility pressure.

Comparing the recoveries from Figures 29(a) and (b) indicates that the maximum utilization (best performance) of the CGI miscible flood occurs up to 0.7 PV injection. The tertiary recovery factor comparisons for further injection show distinct advantage of the 1:1 miscible WAG process. This suggests the use of CGI till 0.7 PV injection and later switching over to the WAG process for maximizing the tertiary recovery. This seems to be the principle behind the patented processes of 'Hybrid WAG' and 'DUWAG' of UNOCAL and Shell respectively, where a large slug of CO_2 (~ 0.6PV) is injected in the reservoir followed by 1:1 WAG.

Yates Reservoir Brine + n-Decane + Berea Core System

Similar WAG and continuous mode gas injection floods were repeated at similar flooding conditions using Yates reservoir brine. The results are included in Figures 30(a) and 30(b) below.

Similar to the previous case of 5% NaCl brine, miscible floods showed significantly higher recoveries than immiscible ones as can be seen in Figure 30(a). The CGI recovery increased from 62.9% to 97.6% and WAG recoveries increased from 28.9% to 72.5% due to miscibility.

The recovery plot of Figure 30(a) favors the use of CGI rather than WAG in both miscible and immiscible cases. However, the use of Tertiary Recovery Factor for comparison, as done in Figure 30(b), shows the benefit of using WAG mode floods in both miscible and immiscible cases. Hence, although the recovery plot shows higher total recovery, WAG floods show better economics, and give maximum benefit in miscible mode.

4.5.2 Effect of Brine Composition in Miscible Tertiary CO_2 Floods

As discussed in the literature review, brine composition could affect stabilization of clays[48] in porous medium, and also influences the waterflood recovery[41][42][44][45]. Hence Craig's rules of thumb were used to infer wettability changes that could have occurred in the displacement tests.

The plots of effect of brine composition on miscible floods are shown in Figures 31(a) and 31(b). As seen in the previous section, the evaluation of the process on the basis of recoveries only can lead to misleading conclusions. Therefore the results are analyzed mainly using the Tertiary Recovery Factor in Figure 31(b).

While in the case of CGI, there appears to be minimal effect of brine composition (according to experiments 3 and 4 in Figure 31(a)), WAG floods showed significant dependence on brine composition. The TRF plot shows that the 5% NaCl brine WAG flood is the best of the miscible floods followed by Yates brine WAG. The CGI floods were comparable and fared lower than the WAG floods.

This can be attributed to the difference in solubility of CO_2 between 5% NaCl brine and Yates reservoir brine. Experiments with natural brine (Paradox Valley Colorado) and pure salt solutions like NaCl, and $CaCl_2$, showed that solubility of CO_2 in natural brines was higher than solubility of NaCl alone. The solubility of CO_2 was shown to be higher in presence of divalent salts from natural brine[63]. This shows that the solubility of CO_2 is higher in natural reservoir brines (like Yates reservoir brine) than pure salt solutions. Hence, relatively higher volumes of CO_2 are available for oil recovery (by dissolution and swelling) in the 5% NaCl brine flood than Yates reservoir brine.

4.5.3 Effect of Core Length

Immiscible gas floods (experiments 1, 2, 5 and 6) were conducted at similar flooding conditions using 5% NaCl Brine and n-Decane on both 1-ft & 6-ft Berea sandstone cores. The results are compared in Figures 32(a) and 32(b) below.

As can be seen in Figure 32(a), the short (1-ft) cores show almost identical tertiary recovery trends for both CGI and WAG Injection, and the final oil recoveries from these tests are comparable. Mitigation of gravity segregation for improved flood profile control with WAG and recoveries are not apparent from the recovery plots. However, the recoveries are significantly different for 6-ft Berea CGI and WAG (33.5% and 54.4%, respectively) floods, suggesting the presence of gravity segregation in the long cores. This agrees with the experimentation that gravity segregation would be more pronounced in the longer cores. This clearly indicates that long core tests are not only appropriate and useful but also essential to examine the effects of the WAG process. Similar trends are also evident in Figure 32(b).

4.5.4 Summarization of Results

The recovery, residual oil saturations and gas utilization factor for the corefloods conducted are summarized in the Table 7 below.

The utilization factor is a good indicator of the overall efficiency of the process, and is a useful augmentation, along with the TRF, for the analysis of the data. The utilization factor for each flood is plotted in Figure 33 below.

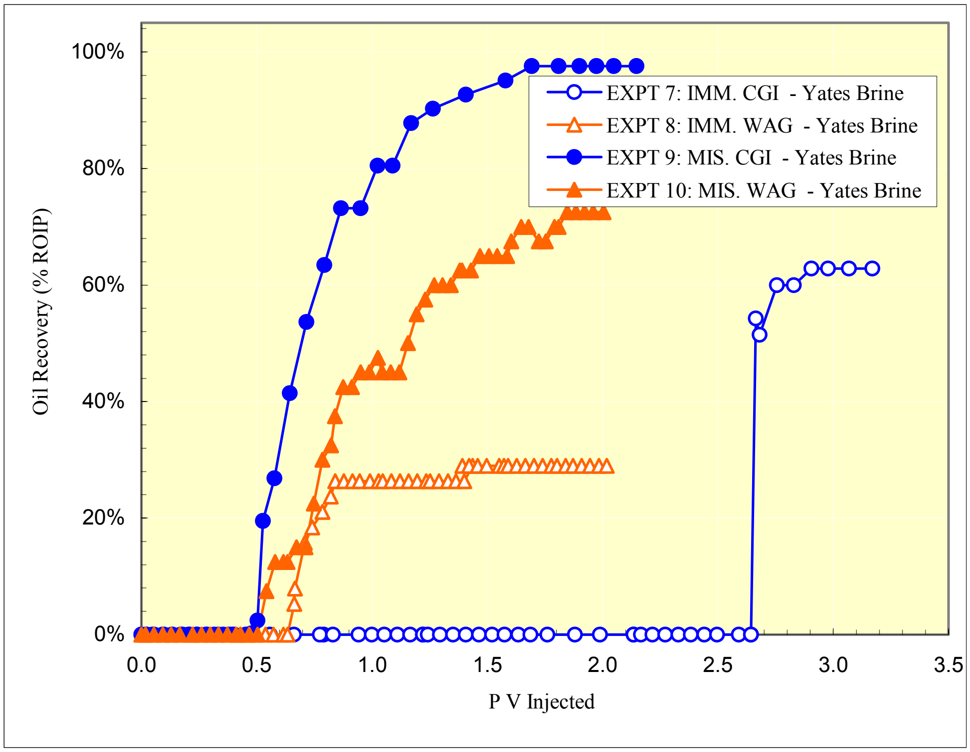


Figure 30(a): Recovery in % of ROIP

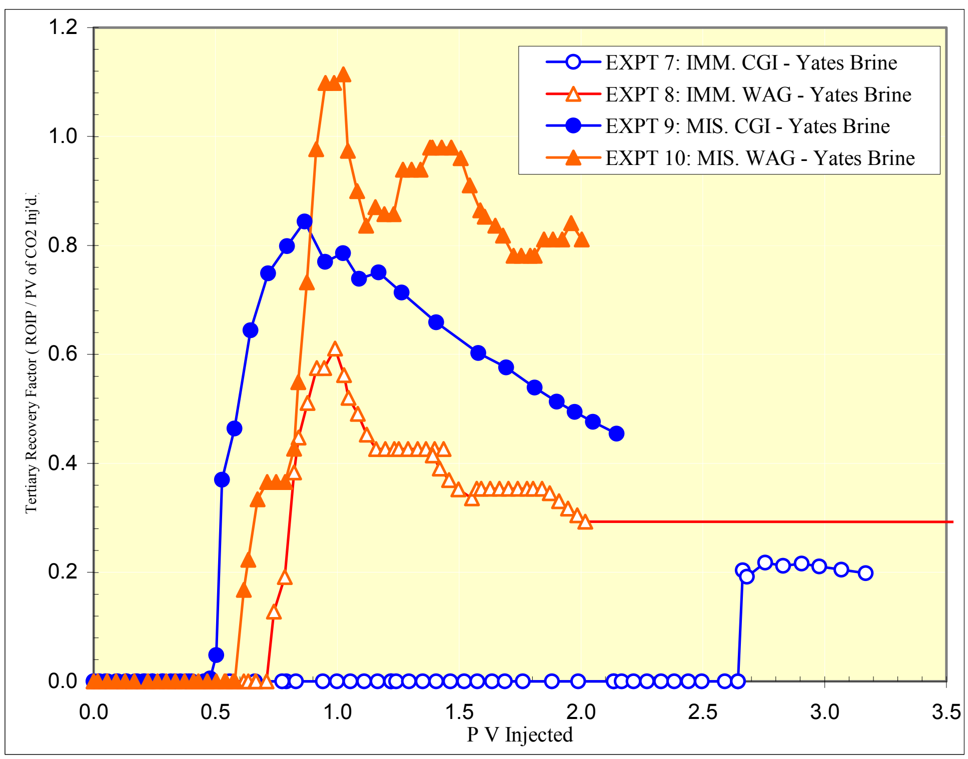


Figure 30(b): Recovery As Fraction of Residual Oil In Place Per PV of CO_2 Injected
Figure 30: Effect of Miscibility and Mode of Injection on tertiary recovery in n-Decane + Yates brine system.

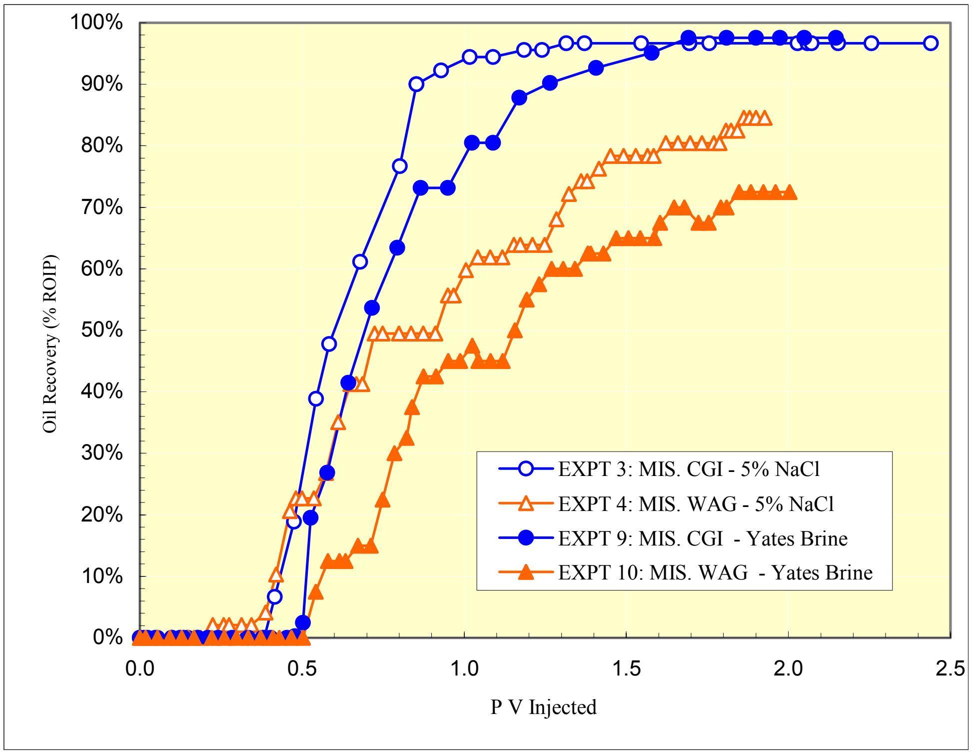


Figure 31(a): Recovery in % of ROIP

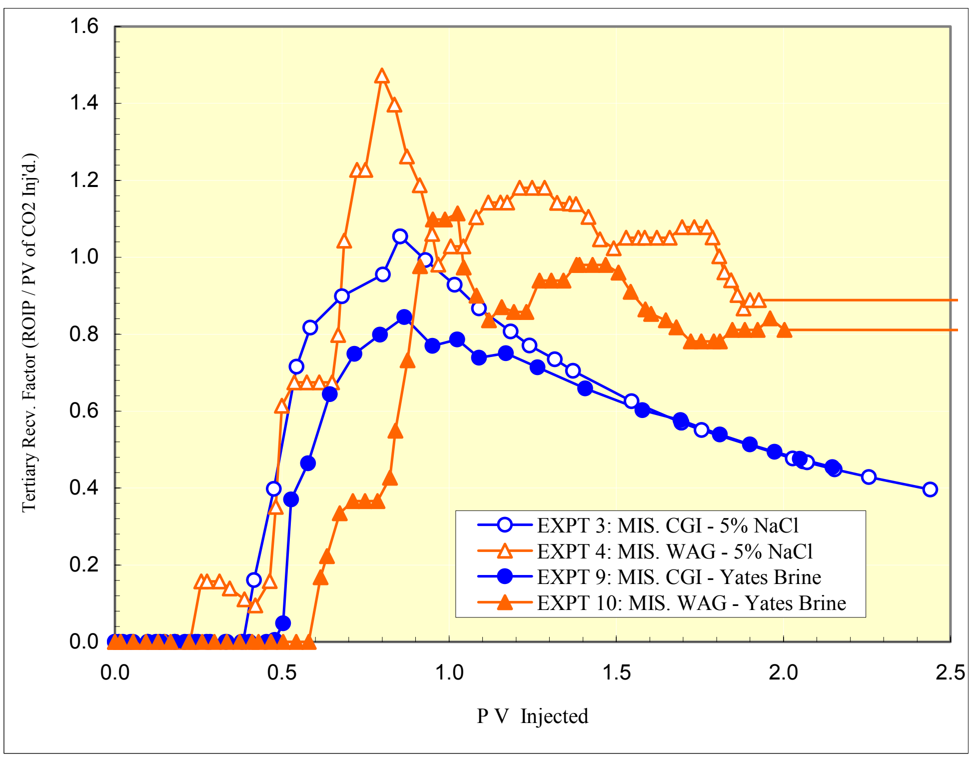


Figure 31(b): Recovery As Fraction of Residual Oil In Place Per PV of CO_2 Injected

Figure 31: Effect of brine composition on tertiary recovery in n-Decane + Yates brine

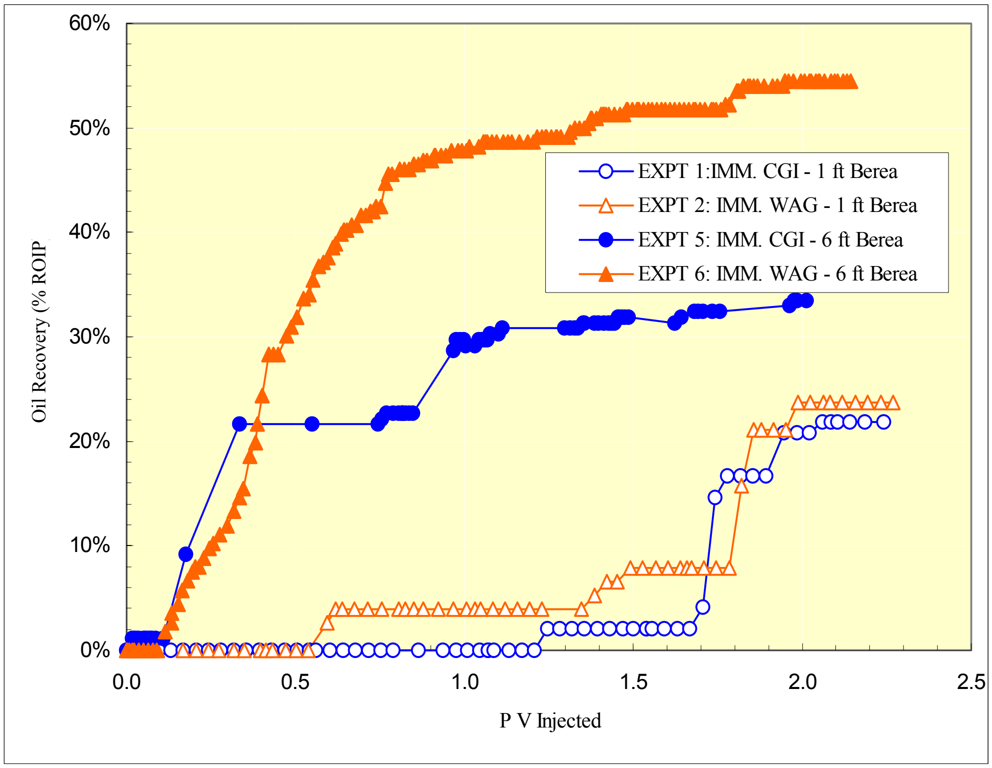


Figure 32(a): Recovery in % of ROIP

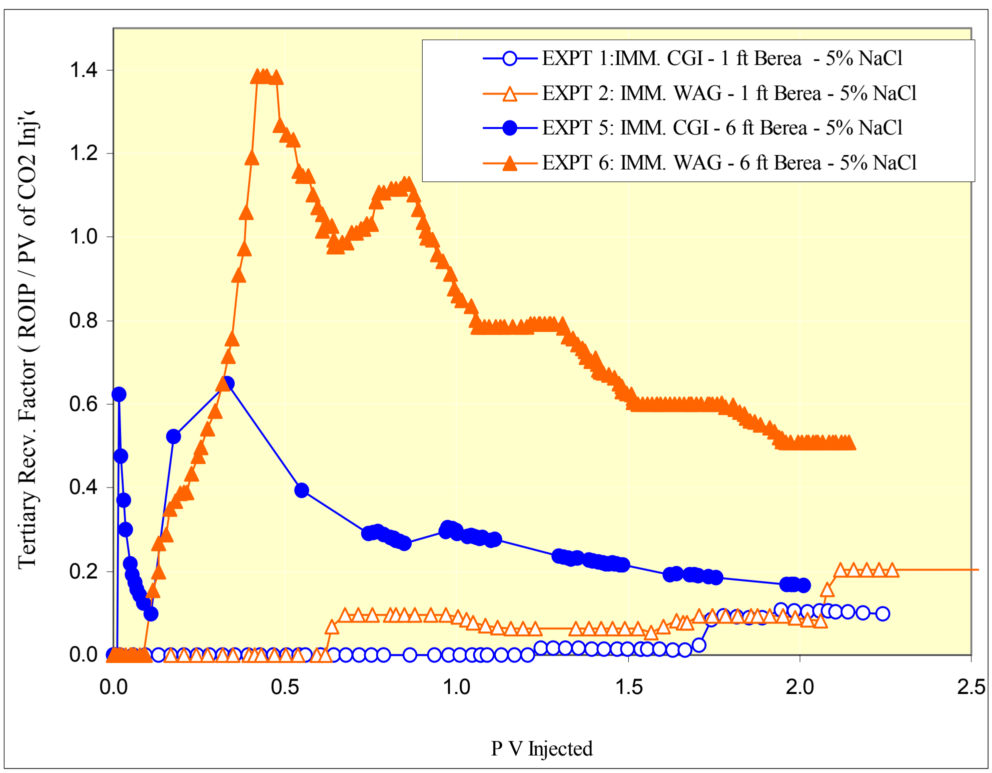


Figure 32(b): Recovery As Fraction of Residual Oil In Place Per PV of CO_2 Injected
Figure 32: Effect of Core length on tertiary recovery in n-Decane + 5% NaCl brine

Table 7: Summary of Tertiary Gas Injection (EOR) Cycles

Expt No.	Experiment Title	P_{TEST} (psi)	S_L	S_G	Rvry (cc)	Rvry %OOIP	Utilz. Ftr. (MCF/bbl)
5 % NaCl Brine + n-Decane + Berea Core							
1	1-ft Immiscible Continuous CO_2	500	47.9	52.1	10.5	8.8%	7.0
2	1-ft Immiscible CO_2 WAG	500	--	--	9	8.3%	4.1
3	1-ft Miscible Continuous CO_2	2500	26.4	73.6	43.5	43.3%	20.2
4	1-ft Miscible CO_2 WAG	2500	--	--	41	42.1%	8.8
5	6-ft Immiscible Continuous CO_2	500	57.1	42.9	62	14.9%	5.8
6	6-ft Immiscible CO_2 WAG	500	--	--	123	26.7%	1.6
Yates synthetic Brine + n-Decane + Berea Core							
1	1-ft Immiscible Continuous CO_2	500	27.8	72.2	22	20.4%	4.7
2	1-ft Immiscible CO_2 WAG	500	--	--	11	9.9%	3.0
3	1-ft Miscible Continuous CO_2	2500	19.8	80.2	40	45.9%	19.4
4	1-ft Miscible CO_2 WAG	2500	--	--	29	35.1%	12.5

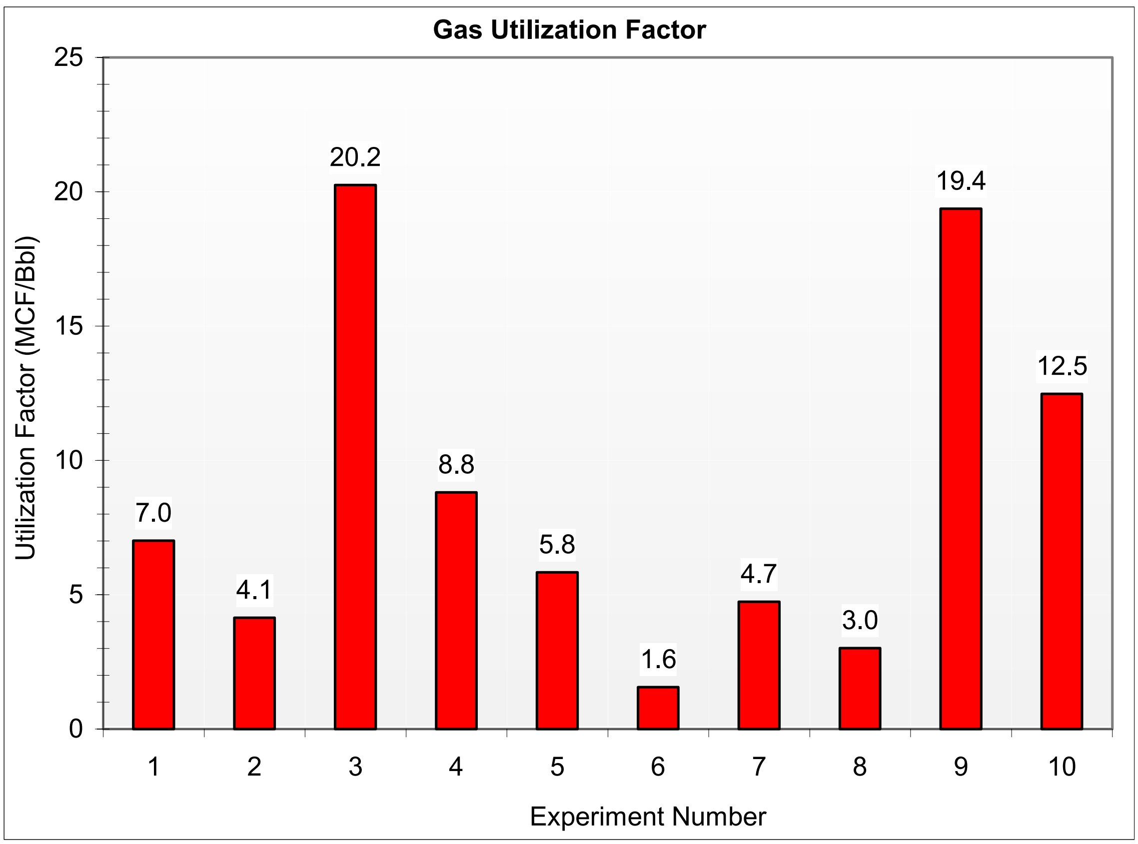


Figure 33: Comparison of Gas Utilization Factor for all the Experiments conducted

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions

Coreflood experiments were conducted with the objective of evaluating miscible and immiscible modes of gas injection, the effect of brine composition and core length on gas-oil displacements in porous media. Berea sandstone was chosen because of its wide acceptance as a relatively homogeneous porous medium well suited for controlled experiments.

Ten sets of experiments – eight with 1-ft Berea cores and two with 6-ft Berea cores have been conducted for this research. Two different brines, one a commonly used 5% NaCl solution and the other actual reservoir brine were used to examine the effects of rock fluid interactions. n-Decane was used as the oleic phase and pure Carbon dioxide as the injected gas. The 6-ft coreflood experiments were conducted using only 5% NaCl brine. Both miscible and immiscible displacements of n-Decane and Carbon dioxide gas were conducted. Miscible floods were performed at 2515 psia and the immiscible ones at 515 psia. Two modes of gas injection were used: Continuous Gas Injection (CGI) and Water-Alternating-Gas (WAG) injection.

Conventional plots of waterflood residual oil recovery vs. pore volume injected were found to yield misleading conclusions. Hence a new factor, namely Tertiary Recovery Factor (TRF) was defined to normalize by pore volume of CO_2 injected the oil recovery. Comparison of the results in terms of TRF enabled the evaluation of the performance of tertiary gas floods on the same basis.

The main conclusions from this study are:

1. The performance evaluation of the gas floods solely on the basis of oil recovery, could lead to misleading conclusions. Recoveries should be normalized by the amount of gas injected to enable direct comparisons.

2. Miscible gas floods were found to recover over 60 to 70% more of the waterflood residual oil than immiscible gas floods. While the recoveries in immiscible floods (both CGI and WAG) were about 23%, the miscible floods yielded 84.5% recovery for the WAG flood and 93.7% recovery for the CGI flood. This is not a surprising result, since laboratory 1D corefloods where sweep efficiency effects are minimal, miscibility has significant impact on oil recovery.

3. Based on oil recovery (as %ROIP), the CGI flood appeared to be better in performance than WAG flood. However, on the basis of the Tertiary Recovery Factor (TRF), where the recoveries were normalized by the volume of CO_2 injected, the WAG flood clearly out-performed the CGI flood. Furthermore, the performance of the CGI miscible flood approaches that of the immiscible gas floods, in terms of TRF, indicating deteriorating economics of the CGI compared to that of miscible WAG flood.

4. The definition of TRF enabled the identification of a process for optimizing tertiary recovery in gas floods. This consists of injecting a continuous gas slug of 0.7 PV (where the CGI flood showed maximum TRF value) followed by 1:1 WAG. This was found to be similar to the patented 'Hybrid WAG' and 'DUWAG' processes employed in the oil industry.

5. Miscible CGI floods showed negligible sensitivity to brine composition variations. Recoveries of 96.7% and 97.6% where obtained with 5% NaCl brine and Yates reservoir brine, respectively. As against this, the miscible WAG recoveries exhibited significant dependence on brine composition. The miscible WAG recoveries showed a significant decrease (12%) in oil recovery when the connate brine was changed from 5% NaCl solution to Yates reservoir brine. While the recoveries for the miscible 5% NaCl brine were 84.5%, the recovery decreased to 72.5% for Yates reservoir brine. This is attributable to the higher solubility of CO_2 in natural multi-component brines than solutions of pure salts like NaCl, which results in higher volumes of CO_2 being available for oil recovery in 5% NaCl brine floods.

6. Both CGI and WAG (with 5% NaCl brine) immiscible experiments showed comparable oil recoveries of 21.9% and 23.7% in 1-ft Berea corefloods, respectively. However, significant differences (~ 21%) in the final oil recoveries of CGI and WAG were seen in 6-ft Berea cores, although the test conditions were identical. The CGI recovery increased from 21.9% in 1-ft Core to 33.5% in the 6-ft corefloods, whereas the WAG recovery showed a higher increase in recoveries, from 23.7% in 1-ft core to 54.4% in 6-ft core. Thus, it was seen that the gravity segregation phenomenon was amplified in long cores, thus making 6-ft corefloods more appropriate and useful to examine the WAG process performance.

5.2 Recommendations

The recommendations from this study for future work are:

1. 1-ft Berea core experiments should be used to identify important parameters affecting gas-oil displacements. The effect of these parameters should then be further examined using the 6-ft coreflood apparatus, as they are time consuming.

2. Berea cores previously exposed to crude oils should not be reused in other displacement experiments due to interfering wettability effects. Use of fresh Berea cores for each fluid pair is recommended.

3. Coreflood test conditions (namely pressure and temperature) should be chosen to avoid the two envelope of the injected gas in order to avoid liquefaction during the tests and to facilitate single-phase fluid transport through the apparatus.

4. The effect of CO_2 solubility in brine on gas-oil displacement should be minimized by using mutually saturated fluids.

5. "Hybrid-WAG" type corefloods should be conducted on long cores to determine the optimum mode for gas floods and to compare their effectiveness against gravity-stable gas floods.

6. Corefloods should be conducted with live reservoir fluids and formation rock samples an at reservoir conditions in order to enable collection of data for field-scale reservoir simulation studies and to facilitate field implementation of promising concepts and processes.

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