

ENHANCED OIL RECOVERY BY SURFACTANT ALTERNATE
CARBONATED WATER INJECTION

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DEDICATION

Specially dedicated to:

My family for their endless support and motivation

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ABSTRACT

Surfactant alternate carbonated water (SACW) injection is a novel mode for enhanced oil recovery (EOR), a method to produce residual oil. This process may overcome the shortcomings that seriously associate carbon dioxide (CO₂) injection such as high CO₂ mobility, viscous fingering and gravity override. Combinations of sodium dodecyl sulfate (SDS) surfactant and carbonated water (CW) system were not used for EOR yet. So, SDS and CW were selected for evaluating wettability, interfacial tension (IFT), and displacement stability. In addition, the oil recovery factor (RF) was evaluated at different reservoir conditions, carbonation levels and SACW injection cycles scenarios. The sessile drop method was used to measure the contact angle in presence of CW, SDS solution and a mixture of CW and SDS at different quartz sandstone reservoir conditions. A sandpack model was utilised for CW, SDS, water flood (WF) and CO₂ flood to measure the displacement instability number (I_{sc}). The obtained results revealed that combinations of SDS and CW system reduce the IFT and contact angle. The IFT values for SDS solution with and without carbonation were 0.2 and 2 mN/m, respectively. The respective contact angles for SDS solution with and without carbonation were 32° and 21.7° at 50°C and 1500 psi. The I_{sc} for CW and WF were 11.6 and 10, respectively, which are considered stable at 60°C and 2750 psi. On the other hand, SDS and CO₂ flood processes revealed unstable displacement. Moreover, low pH of CW system depicted a significant change in the SDS adsorption on the glass beads as compared to non-CW system. The 100% CO₂ content, reservoir temperature of 60°C and pressure of 2750 psi increased RF up to 83.05, 84.42 and 85.22%, respectively. The highest RF was 86.58% which procured from the largest SDS slug scenario. In conclusion, SACW may have a positive impact on the recoverable oil and it can display a technical knowledge to study other techniques for EOR.

ABSTRAK

Suntikan air berkarbonat bersilih ganti dengan surfaktan (SACW) ialah mod baharu untuk perolehan minyak tertingkat (EOR), kaedah untuk pengeluaran minyak baki. Proses ini mungkin boleh mengatasi kelemahan yang serius berkaitan suntikan gas karbon dioksida (CO₂), misalnya pergerakan CO₂ yang tinggi, jejarian likat dan songsangan graviti. Gabungan sistem surfaktan natrium dodesil sulfat (SDS) dan air berkarbonat (CW) belum pernah diguna kan dalam EOR. Oleh itu, SDS dan CW dipilih untuk menilai kebolehbasaan, tegangan antara muka (IFT), dan kestabilan anjakan. Di samping itu, faktor perolehan minyak (RF) dinilai pada keadaan reservoir berbeza, tahap pengkarbonatan dan senario kitaran suntikan SACW. Kaedah titis sesil telah digunakan untuk mengukur sudut sentuh dengan kehadiran CW, larutan SDS dan campuran CW dan SDS pada keadaan reservoir pasir kuarza yang berbeza. Model pek pasir digunakan bagi CW, SDS, banjir air (WF) dan banjir CO₂ untuk mengukur nombor ketidakstabilan anjakan (I_{sc}). Keputusan yang diperoleh menunjukkan bahawa gabungan sistem SDS dan CW boleh mengurangkan IFT dan sudut sentuh. Nilai-nilai IFT untuk larutan SDS dengan dan tanpa pengkarbonatan masing-masing ialah 0.2 mN/m dan 2 mN/m. Sudut-sudut sentuh bagi larutan SDS dengan dan tanpa pengkarbonatan masing-masing ialah 32° dan 21.7° pada 50°C dan 1500 psi. Nilai I_{sc} bagi CW dan WF masing-masing ialah 11.6 dan 10, yang didapati stabil pada 60°C dan 2750 psi. Walau bagaimanapun, proses banjir SDS dan CO₂ menunjukkan anjakan yang tidak stabil. Selain itu, sistem CW dengan nilai pH yang rendah menunjukkan perubahan yang ketara terhadap penjerapan SDS pada manik kaca berbanding sistem tanpa CW. Sistem dengan 100% kandungan CO₂, suhu reservoir 60°C dan tekanan 2750 psi telah meningkatkan RF masing-masing kepada 83.05%, 84.42%, dan 85.22%. Nilai tertinggi RF ialah 86.58% yang diperoleh daripada senario slug terbesar SDS. Kesimpulannya, SACW mungkin boleh memberi kesan yang positif terhadap perolehan minyak dan ia boleh menunjukkan pengetahuan teknikal untuk mengkaji teknik lain dalam EOR

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LIST OF ABBREVIATIONS

C^*		Wettability number, dimensionless
D	-	Sand pack diameter, cm
V	-	Displacing of Darcy velocity, m/day
μ_2	-	Oil viscosity, cp
μ_w	-	Water viscosity, cp
α	-	Interfacial tension, mN/m
K	-	absolute permeability, md
I_{sc}	-	Instability number, dimensionless
P	-	Pressure, psi
R	-	0.08314467 bar l/mol K (universal gas constant)
T	-	Temperature, °C
ρ_o	-	Oil density ,gm/cc
ρ_w	-	Water density, gm/cc
GOR	-	Gas oil ratio, m ³ /m ³
PV	-	Pore volume, %
t	-	Time, min
RF	-	Recovery factor, fraction
CWI	-	Carbonated water injection
M_x	-	CO ₂ solubility, mole/Kg
M_1	-	The molality of dissolved Sodium in brine water, mole/L
	-	The molality of dissolved Potassium in brine water, mole/L
	-	The molality of dissolved Calcium in brine water, mole/L
	-	The molality of dissolved Magnesium in brine water, mole/L
	-	The molality of dissolved Chloride in brine water, mole/L
	-	CO ₂ mole fraction, fraction
	-	The fugacity coefficient
	-	Standard chemical potential

- Constant
- Constants
- water vapor pressure, psi
- Critical pressure of water, psi
- Critical temperature, °K or °C
- Critical pressure, psi
- Constants
- Initial concentrations, mg/L
- equilibrium concentration, mg/L
- surfactant solution volume, L
- weight of the glass beads (adsorbent), gm
- Adsorption, mg/g
- Porosity, %
- Length of the porous media, cm
- Change in pressure over the media, atm
- Cross-sectional area across which flow occurs, cm²
- Flow rate through the porous medium, cc/s
- Flow rate through the porous medium, cc/s
- Permeability, md
- Viscosity, cp
- Contact angle, degree
- Differential oil production volume at (), cc
- Oil production volume at (), cc
- Oil volume at (), cc
- Differential time at (), min
- Time at ()
- Time at (), min
- Oil flow rate at, cc/min

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CHAPTER 1

INTRODUCTION

1.1 Overview

Enhanced Oil recovery (EOR) may be generally a technical term for all processes that utilize to enhance oil production, it can be applied after the primary production operations (Kokal and Al-Kaabi, 2010; Khan and Islam, 2007). In the last decade, EOR was received more attention mainly as a result of increasing the price of crude oil as well as the high significant quantities of recoverable crude oil that present in the reservoirs (Ko *et al.* 2014). In other words, all of the oil reservoirs are discovered might be candidate for EOR implementations as a result of the reservoirs still contain huge amount of crude oil (Wall and Archer, 1986). The sequences of the oil production scenarios follow primary depletion, secondary recovery and finally tertiary recovery operations (Khan and Islam, 2007). Furthermore, there is about 20 to 50% of oil that can be recovered by primary and secondary methods (Park *et al.* 2015). These methods are utilized in sequence.

Consequently, the utilization of chemical materials such as surfactants and carbon dioxide (CO₂) gas can be used for EOR (Jangda *et al.* 2014). The surfactant significantly improves oil recovery. However, the adsorption of surfactant on the reservoir rock decreases the amount of surfactant in the aqueous phase. Similarly, CO₂ gas has a particular effectiveness in recovering oil as well (Jangda *et al.* 2014).

Chemical flooding is a common term for injection operations which utilize particular chemicals such as surfactants that dissolved in the injection water for a purpose of improving oil recovery. The tertiary recovery scheme of surfactant flood that has been highly pursued throughout the past decades because of its ability to effect on the oil-water-interfacial tension and wettability alteration of the reservoir rock from an oil-wet surface to water-wet surface to extract the oil that remains trapped in the

formation (Hou *et al.* 2015; Alotaibi *et al.* 2011). The one of the essential parameters of the reservoir physical property is the wettability. This parameter may have an effect on the aqueous phase relative permeability, oil recovery, waterflooding characteristics and the residual oil allocation. Therefore, several operations need to be assessed in order to modify the reservoir rock wettability for EOR (Thomas, 2008; Morrow, 1990; Golabi *et al.* 2012; Hou *et al.* 2015). Therefore, the injection of surfactant solution into the reservoir can reduce the interfacial tension (IFT) between brine water and residual oil (Rosen, 2004) from the original value of 30mN/m to about 0.001mN/m which causes to decrease the capillary force (Hirasaki *et al.* 2011). This interfacial tension value might split up the oil into tiny droplets that can be displaced from the rock pores by water.

Carbonated water flooding is another emerging EOR technique that utilize limited amount of CO₂ dissolved in the injection water. CO₂ gas has been implementing in many depleting oil reservoirs across the world to improve oil recovery for more than 30 years (Kechut *et al.* 2010). There are two methods can be used for CO₂ injection (Kechut *et al.* 2011). Firstly, gas-based method, in which CO₂ may be continuously injected in one rich phase or water alternating gas (WAG) injection. This technique requires very large quantities of CO₂. Furthermore, the CO₂ supercritical condition is normally injected which is above the critical temperature and pressure of 31.1 °C and 1030 psi, respectively. The secondly method is called water-base method, the CO₂ gas may be dissolved in brine water injection firstly, thereafter, the solution is injected into the reservoir followed by water flooding process. This technique scheme is known as carbonated water injection (CWI) (Kechut *et al.* 2011). Currently, some active research pursues in this area with the rationale that CWI can reduce gravity segregation encountered in conventional WAG processes. In this technology, CO₂ is dissolved in water until the solubility limit is reached depending upon pressure, temperature, and injection water salinity, thereafter the obtained carbonated water is then injected into the reservoir as EOR mode. Solubility of CO₂ in water decreases with increasing temperatures, it increases with increasing pressures, and it decreases with increasing water salinities.

1.2 Problem Statement

Surfactant alternating carbonated water (SACW) is a novel mode which had never used for EOR yet. Some significant shortcomings may seriously associate with the tertiary process of CO₂ injection such as high CO₂ mobility, and viscous fingering (Bakhtiyarov *et al.* 2007; Jangda, 2014). In addition, gravity override issue, CO₂ can tend to move to the top of formation and override the displaced fluids as a result of density difference between CO₂ and other fluids. Therefore, this gravity effect is exploited by flooding from the top of the reservoir and displacing fluids down dip. These problems lead to earlier breakthrough and very poor macroscopic and microscopic sweep efficiencies. Thus, these phenomena might cause of the residual oil to be inaccessible to the injected CO₂ and it is trapped by water. The improvement of well injectivity can be developed by surfactant alternating gas injection (SAG) as a result of gas mobility reduction at the flood front (Farajzadeh *et al.* 2016). However, the mobility of gas is high at the displacement contact between fluids because the viscosity of gas is less than viscosity of surfactant solution slug. Consequently, the instability of free gas slug can occur at earlier life of the process which leads to viscous fingering becomes high at flood front, early breakthrough, low recovery factor and slug of gas may be dramatically collapsed due to high gas velocity (Jangda, 2014). So, this issue can be severed when the water and oil viscosity ratio is unacceptable.

In addition, natural reservoir pressure depletion of trapped fluids is another factor that influences the oil production rate due to hydrocarbons extraction continuously during primary recovery method (Meyer, 2007). The natural pressure of the reservoir may be declined to a particular value. Consequently, the remaining crude oil cannot be pushed by the slug towards production side anymore (Terry, 2001; Donaldson *et al.* 1989; Park *et al.* 2015). This issue needs to be assessed by usually secondary and tertiary recoveries method such as chemical flooding process (Thomas, 2008; Jamaloei, 2009).

Furthermore, the high IFT between immiscible fluids of water and oil into the reservoir is one of the most important factors that substantially cause trapped oil into the pours media. Consequently, the water and oil saturations and displacement process

are drastically effected by IFT. On the other hand, SACW technique may overcome these issues and restrict the mobility of the displacing fluid.

There is a significant surfactant adsorption on the rock surface during surfactant solution flooding causes to strip surfactant from the aqueous phase which leads to decrease the performance of the system (Iglauer *et al.* 2010; Park *et al.* 2015; Thomas, 2008; Jamaloei, 2009). Thus, the surfactant content into the slug may be lessened (Ibrahim, 2006). So, this is considered significantly unfavorable phenomenon as well.

There are few published data evaluating the performance of CWI under various conditions and injection scenarios which are carried out under consistent experimental conditions. Moreover, the capacity of the CWI technique to permanently store the injected CO₂ is still a challenge and requires more detailed studies to investigate the effect of various conditions on the CO₂ storage capacity of CWI.

To the best of my knowledge, the combination of sodium dodecyl sulphate (SDS) surfactant solution and carbonated water was selected in this study work for EOR purpose. For the aim, this research firstly may depict the influence of SDS solution and carbonated water mixture on the IFT and wettability alteration. In addition, the SACW was experimentally applied for packed sandstone porous media in order to study the effectiveness of carbonation level, reservoir pressure and temperature on the recovery factor. The SACW were applied to investigate the effectiveness of slug sizes of SDS solution and carbonated water on the oil recovery factor. The impact of combination of SDS solution and carbonated water on the recovery factor has not been comprehensively investigated yet. No reported simulation work or experimental study has been published for this oil recovery technique yet. It may depict a positive impact for EOR. Furthermore, the reasonable CO₂ solubility range into the injection brine water needs to be achieved when CW utilizes for EOR. An experiment study of SACW process for a sandpack sample should thus be undertaken in order to indicate if the proposed EOR is technically feasible.

1.3 Objectives

Based on the above referred problem statements, consequently, the objectives of this research are as follows:

1. To determine the wettability behaviour, IFT reduction and instability displacement of surfactant and carbonated water system at reservoir conditions.
2. To evaluate the feasibility and oil recovery efficiency of SACW flooding in quartz sand porous media.
3. To determine the optimal oil production strategy using different SACW injection scenarios.

1.4 Scope of Research Study

To achieve the objectives, the scope of this study included the following:

1. Interfacial tension measurement was carried out in room condition since there is no suitable equipment that can be used to determine the IFT in reservoir conditions. A set of carbonated water was prepared in high pressure and temperature condition' and the pressure' were gradually decreased until room conditions. Therefore, the determination of IFT between oil and brine water was conducted with different surfactant concentrations and different salinity concentrations of 10,000, 20,000 and 30,000 ppm at ambient condition. In addition, the determination of IFT between oil and carbonated water was conducted with different surfactant concentrations and different salinity concentrations such as 10,000, 20,000 and 30,000 ppm at ambient condition.
2. Determination of surface tension of brine water was carried out with different surfactant concentrations and different salinity concentrations of 10,000, 20,000 and 30,000 ppm at ambient condition.

3. The investigation of fluid displacement instability index such as water flooding, surfactant flooding, carbonated water flooding and CO₂ gas flooding was conducted at reservoir conditions.
4. The sessile drop method was used for wettability measurements as follows:
 - a) The contact angle between crude oil, carbonated water and quartz sandstone was investigated at several temperatures (40°C, 50°C and 60°C), but at constant salinity and pressure of 30,000 ppm and 2000 psi, respectively. In addition, contact angle was measured at saline water concentrations of 30,000 ppm and 10,000 ppm, while temperature and reservoir pressure were constant at 40°C and 2000 psi respectively.
 - b) The contact angle between crude oil, carbonated water and quartz sandstone was measured at several concentrations (0.0%, 50% and 100%) of carbonation level, but at constant temperature, salinity, and reservoir pressure of 60°C, 30,000 ppm and 2000 psi, respectively.
 - d) The contact angle between crude oil, carbonated water mixed with solution of SDS concentration of 0.01wt% and quartz sandstone was examined at temperature of 40°C, 50°C and 60°C, salinity of 30,000 ppm and reservoir pressure of 1500 psi. In addition, a new model was generated for this work.
5. The oil flow rate and oil recovery factor were investigated during SACW and the effectiveness of some important parameters on improvement oil recovery factor were studied as follows:
 - a) CO₂ concentration effect was run at 0.0, 50, 100%
 - b) Reservoir pressure effect was run at 1500, 2100 and 2750 psi
 - c) Reservoir temperature effect was run at 40°C, 50°C and 60°C
 - d) Tertiary mode effect of SACW cycles:
 - i. First experiment: (Three cycles, each cycle contains slug size ratio of 0.25PV CW and 0.75PV surfactant)
 - ii. Second experiment: (Three cycles, each cycle contains slug size ratio of 0.50PV CW and 0.50PV surfactant)
 - iii. Third experiment: (Three cycles, each cycle contains slug size ratio of 0.75PV CW and 0.25PV surfactant)

1.5 Significant of the Study

Since the SACW is a new technique and may viable option for EOR. Therefore, this proposed study intends to exhibit the ambiguity about dependence of oil recovery on SACW cycles particularly at different CO₂ ratios in water (GWR) and to assess the ability of the process to produce a tertiary oil recovery from a sandpack core sample. In addition, the purpose of flooding cycle schemes is to reduce CO₂ velocity into pore space which leads to improve areal and vertical sweep efficiency and may procure the greatest potential impact on recovery factor (Pritchard and Nieman, 1992). Consequently, this study shall depict to what extend the effective of this process for incremental oil recovery.

Moreover, carbonated water has additional values in addition improving residual oil recovery. An added positive merit on carbonated water is the process of storing CO₂ gas that contained in the carbonated water into rock formation. The process of sequestration of CO₂ into a mineral solid would be done simultaneously with the introduction of carbonated water. Thus, this becomes another option of carbon capture and storing which ideally improve both oil recovery and nature conservation. This significance of carbonated water injection will surely become a factor of attraction in application of carbonated water in maturing field.

In addition, the use of SACW injection for EOR purpose is a new task in petroleum engineering and it needed to be examined and validated prior to it implemented in a full field scale. SACW usage for EOR faces with a huge question that is how combination of carbonated water and surfactant solution has an advantage for EOR process. This depicts that CO₂ is trapped into the porous media which causes water/oil IFT reduction and oil mobilization at low saturation. So, the residual oil saturation is effectively reduced. Therefore, these phenomena may enhance surfactant flooding and reflect a positive impact on the surfactant solution performance instead of additional any other chemicals. Therefore, the SACW might be undertaken in order to diminish surfactant amount and to avoid utilizing chemical materials that associate surfactant flooding such as alkaline and polymer.

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