

King Fahd University of Petroleum and Minerals



A Numerical Investigation of Wettability Alteration during Immiscible CO₂ Flooding Process

This is part of a PhD thesis being conducted at Petroleum Engineering Department
by

**Saad M. Al-Mutairi, PhD Student
ID#965189**

Supervised by

**Dr. Sidqi A. Abu-Khamsin, Professor
Dr. M. Enamul Hossain, Assistance Professor**

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Abstract

Wettability has been recognized as one of the controlling parameters of the remaining oil-in-place. The knowledge of wettability alteration is essential to understand the displacement mechanisms and to recover oil efficiently. Continuous alteration of wettability and other related properties need to be addressed properly for an effective approach to enhance oil recovery significantly. Literature review showed that extensive research was devoted to laboratory experiments including core and micro-model flooding to investigate wettability alteration during CO₂ flooding. However, limited research on numerical and/or analytical modeling was reported where continuous alteration phenomena are addressed properly. Moreover, to the best of our knowledge, published numerical and/or analytical models and their solutions are time-independent. Ignoring this important time dimension creates a significant knowledge gap on the numerical and/or analytical modeling and their solutions in reality. To mitigate the shortcomings associated with the existing modeling approaches, A novel way of determining the Corey relative permeabilities of the oil and CO₂ phases as functions of wettability was developed to handle wettability alteration continuously during CO₂ flooding process. A two-phase immiscible simulation model was built numerically utilizing MATLAB program. This study showed that the inclusion of wettability alteration is very influential parameter in enhancing oil recovery and sweeping the reservoir efficiently.

Introduction

Wettability is the relative preference for adhesion of two fluids to a solid surface (Donaldson and Alam, 2008). The tendency of a liquid to spread over a solid surface can be expressed more conveniently and in more precise nature by

measuring the angle of contact at the liquid-solid surface (Cole, 1969). The conventional means of measuring the reservoir rock's wetting state is by contact angle, θ (Agbalaka et al., 2008). The contact angle is measured through the denser liquid phase and ranges from 0 to 180° (Amyx et al., 1960). Knowledge of the reservoir wettability is essential to develop good understanding of the displacement mechanisms and to recover oil efficiently. Wettability has been recognized as one of the controlling parameters of the remaining oil-in-place (Alotaibi et al., 2010). There are four conditions of wettability: water-wet, oil-wet, fractional-wettability and mixed-wettability.

Wettability alteration is an effective approach to enhance oil recovery significantly. Four main factors affecting wettability alteration which are: oil composition, brine chemistry, rock surface mineralogy and the system temperature, pressure and saturation history (Buckley et al., 1998). The adsorption of polar compounds and/or the deposition of organic matter that was originally in the crude oil can alter most of the rock surface mineralogy. The polar compounds contain a polar end and a hydrocarbon end. The polar end adsorbs on the rock surface, exposing the hydrocarbon end and making the surface oil wet (Anderson, 1986). Brine chemistry plays a major role in altering the wettability of the rock. The salinity and pH of brine strongly affect the charge of the rock surface. The rock surface becomes positively charged when the pH is decreased and the rock surface becomes negatively charged when the pH is increased. Increasing temperature and pressure tends to increase the solubility of wettability-altering compounds. In an oil-bearing formation, the wettability can vary with depth, with a greater water-wetting preference near the bottom of the transition zone and a greater oil-wetting preference near the top (Okasha et al., 2007). The higher zones have a greater capillary pressure, which can counteract the disjoining pressure and destabilize the

water film, allowing surface-active components in the oil to contact the solid. Lower in the structure, the solid surfaces mostly retain the water film (Oilfield Review, summer 2007).

This work reveals the importance of inclusion wettability alteration during the immiscible CO₂ flooding process. A novel way was developed to calculate the relative permeability of oil and CO₂ as a function of contact angle. A new model of contact angle with respect to exposure time to CO₂ was developed and incorporated in the displacement model.

Literature Review

Wettability alteration during CO₂ flooding process is investigated extensively in the literature through laboratory experiments and simulation models. Researchers measured the wettability before and after CO₂ flooding process in order to track any changes in wettability (Lin and Huang, 1990; Stalkup, 1970; Shelton and Schneider, 1975; Tiffin and Yellig, 1983). Water blocking of CO₂ has not been found to be a problem in mixed wet and oil-wet formations (Spence and Ostrander, 1983; Tiffin et al., 1991; Magruder et al., 1990).

Wettability alteration has been addressed heavily in the literature. Most of the research work was carried out through laboratory experiments including core flooding and micro-models. In contrast, limited numbers of numerical/analytical models were reported to investigate the influence of wettability during CO₂ flooding. Table 1 presents four widely accepted models handling the wettability alteration.

First, Van Dijke and Sorbie (2002) studied wettability effects through pore-scale network simulator models in three-phase porous media. The wettability was

specified by the cosine of the oil-water contact angle ($\cos \theta_{ow}$) where the sign of this quantity indicated the wetting order of the fluids (oil and water) in the pore. The capillary pressure in three-phase porous media was measured through the Young Laplace equations. The relations for the contact angles for each possible fluid-fluid interface with the solid were combined to develop a constraint on the three-phase contact angles and IFT (Bartell and Osterhof, 1927; Johnson and Dettre, 1993; Zhou and Blunt, 1997). The wettability of the pore was represented in the pore-scale network simulator by measuring the contact angles.

Second, Delshad et al. (2006) developed a new mathematical model to evaluate wettability alteration for a naturally fractured reservoir. Surfactants were used to change the wettability by increased imbibition of the water into the matrix rocks. Wettability alteration was modeled through measuring the changes in relative permeability and capillary pressure.

Third, Farhadinia and Delshad (2010) modeled wettability alteration by chemical injection in naturally fractured reservoirs using dual porosity MINC (multiple interacting continua) method. Fractures are connected network while the matrices are discrete volumetric elements like sugar cubs. Two flow equations were applied, one for the matrix and another for the fracture. The two flow equations were tied through a transfer function. Two sets of relative permeabilities were required to model input corresponding to the initial and final wettability states for the rock. The relative permeability in each gridblock was calculated. Relative permeabilities corresponding to the two extreme wetting states were represented by k_{rl}^{final} and $k_{rl}^{initial}$. The relative permeabilities for each phase were assumed. As a function of wettability, the capillary was modeled linearly. Then, the capillary pressure was scaled with IFT. The transfer function was calculated by solving the water pressure

equation of the matrix. The transfer terms were added to the fracture pressure equation to solve the fracture pressure equation implicitly. At the end of each time step, the fracture and matrix variables were obtained. The wettability alteration model updated the relative permeabilities and capillary pressures as an input parameter. Forth, Ju et al. (2010) developed a new mathematical model handling wettability alteration. It was assumed that relative permeabilities would be affected due to asphaltene deposition. Thus, relative permeabilities would be modified.

As can be noticed clearly, the solutions of these numerical/analytical models are time-independent. Also, rock and fluid properties are considered to vary with space only (Hossain et al., 2008). Although time is a very crucial factor in evolution of any rock and fluid property, it is absent in all solutions of these models. This shortcoming creates a significant knowledge gap between the analytical/numerical solutions and reality. Therefore, bridging this gap through development of a time-dependent model to trace the wettability alteration during CO₂ flooding process is very useful.

CO₂ Flooding

When oil recovery is not efficient with water injection, tertiary process is needed in order to enhance oil recovery through altering the rock wettability. CO₂ flooding is one of a well-known EOR method established in the early 1960s. It is considered one of the most applied EOR processes around the world along with thermal injection. CO₂ floods in North America are the only EOR projects, besides hydrocarbon gas floods, that have consistently and significantly increased annual EOR production since the 1986 crash in oil prices (Jarrell et al., 2002). The American Petroleum Institute stated that the oil and gas industry has over 35 years of continuously developing experience in transporting and injecting CO₂ for

enhanced oil recovery. There are two types of oil displacement mechanisms by CO₂: Miscible and immiscible Displacements. Miscible displacement occurs when two fluids can be mixed together in all proportions and all mixtures remain in a single phase (Stalkup, 1984). On the other hand, immiscible displacement occurs when two distinct fluid phases are apparent, separated by a sharp interface (Stalkup, 1984).

The immiscible CO₂ flooding process has considerable potential for the recovery of moderately viscous oils, deep reservoirs and thin formations which are unsuited for the application of thermal recovery techniques (Dyer and Farouq Ali, 1989). Three mass transfer mechanisms are usually occurred during the immiscible CO₂ flooding process: solubility, diffusion and dispersion effects. The Solubility is a function of temperature, pressure and water salinity (Lake 1989). For low pressure application (<7 Mpa), the major effect would be the solubility of carbon dioxide in crude oil (Klins 1984). CO₂ is more soluble in hydrocarbons as a gas rather than a liquid phase (Holm 1959, Briggs and Puttagunta, 1984). The CO₂ solubility increases as pressure increases and temperature decreases (Crawford et al., 1963). The CO₂ increases the viscosity of water slightly (Tumasyn et al., 1969) and decreases the density (Parkinson and de Nevers, 1969). Diffusion is the macroscopic transport of mass, due to random molecular motions, and is independent of any convection within the system (Crank 1967, Rojas 1985). Diffusion helps carbon dioxide penetrate into heavy oil which may help to reduce gravitational and viscous instabilities (Dyer and Farouq Ali, 1989). Dispersion is an additional mixing of fluid occurs in the porous medium due to velocity (Dyer and Farouq Ali, 1989). This additional mixing is due to the dispersive force of attraction which occurs in highly polarizable molecules such as hydrocarbons (Laidler and Meiser, 1982).

When oil is exposed to CO₂, oil properties will be changed. Literature highlighted four main changes to the oil properties: oil viscosity reduction, swelling factor, interfacial tension reduction and asphaltene precipitation. First, the viscosity of oil saturated with CO₂ is a function of temperature, pressure and concentration of dissolved CO₂ (Dyer and Farouq Ali, 1989). Huge reduction of oil viscosity is occurred at lower operating temperature (Rojas and Farouq Ali, 1985). Second, crude oil swells when contacted with CO₂. The amount of swelling increases with increased CO₂ solubility (Dyer and Farouq Ali, 1989). Swelling factors increase dramatically at pressure below the CO₂ bubble point pressure (Briggs and Puttagunta, 1984). Third, the interfacial tension of oil is reduced in the presence of CO₂ (Beecher and Parkhurst, 1926). The interfacial tension decreases moderately with increasing carbonation pressure of brine (Rojas and Farouq Ali, 1985). Fourth, asphaltene precipitation can cause serious problems in the reservoir. Asphaltene precipitation occurs when the hydrocarbons and polar fractions lose their ability to disperse colloiddally the asphaltene fraction (Strausz 1979). As the CO₂ pressure is increased, the tendency for asphaltene to flocculate from toluene solution in heavy oil increased (Fuhr et al., 1985). The asphaltene precipitation is decreased as temperatures were raised (Dyer and Farouq Ali, 1989).

Piloting immiscible CO₂ flooding process was implemented in late 1940s in US. The first full scale of immiscible CO₂ flooding process was conducted in Bartlesville in Oklahoma in 1958 with carbonate water injection (Dyer and Farouq Ali, 1989). The first Pure CO₂ gas injection was conducted in the Ritchie field of southern Arkansas in 1969 (Khatib and Earlougher, 1981). Outside the US, immiscible CO₂ flooding is conducted in the Bati Raman in Turkey in 1980 (Mutairi and Kokal, 2011). This project is considered one of the most successful EOR applications in the history for heavy oil fractured carbonate reservoirs.

New Modified Corey Relative Permeability Model

Phase relative permeability relationship is vital parameter in assessing the recovery efficiency for a particular field. Normalized phase saturation is a well-established representation of phase relative permeability and can be expressed as:

$$S_{on} = \frac{(S_o - S_{or})}{(1 - S_{or} - S_{wi})} \quad (1)$$

The power law model presented earlier is often called the "Corey model" even though it is not the same as the model originally presented by A. T. Corey in 1954 (Lake, 1989). The power law model for relative permeability of oil and gas can be expressed as:

$$k_{ro} = k_{ro}^o S_{on}^{no} \quad (2)$$

$$k_{rCO_2} = k_{rg}^o (1 - S_{on})^{ng} \quad (3)$$

As proven experimentally by several researchers that maximum oil recovery apparently occurs in neutral or slightly oil-wet cores during the core flooding experiments. The maximum oil recovery in the oil-wet rocks was achieved because the oil is located in small pores resulting in higher residual oil saturation and the recovery factor becomes less if the residual oil saturation is decreased as in the intermediate-wet rocks. Based on this knowledge, it is acceptable to say that residual oil saturation will be in exponential relationship with the rock wettability which means that the residual oil saturation will drop exponentially as the rock wettability changed from oil-wet to intermediate-wet as shown in figure-1.

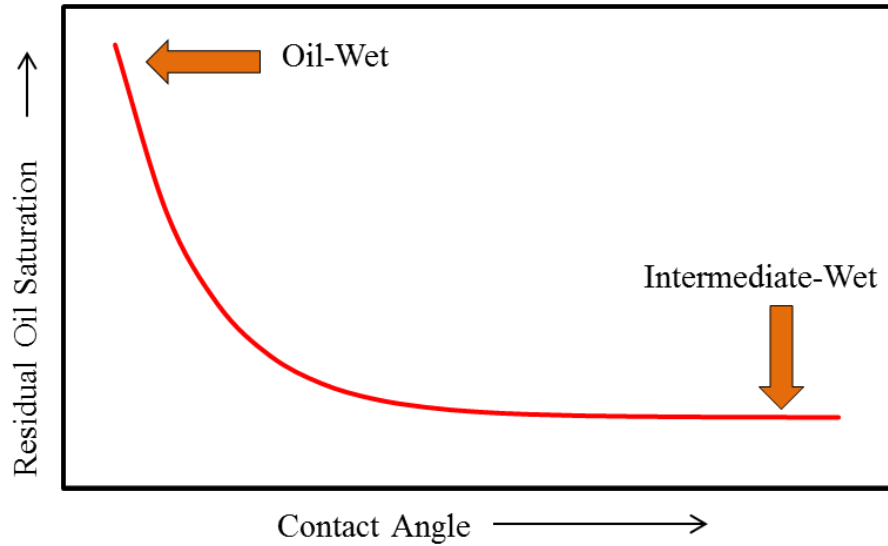


Figure-1: Expected profile of residual oil saturation vs. contact angle

In our study, assumption was made to have a system which is initially strongly oil-wet. Then, the system was exposed to CO₂ injection converting the system wettability to intermediate-wet as seen in figure-2.

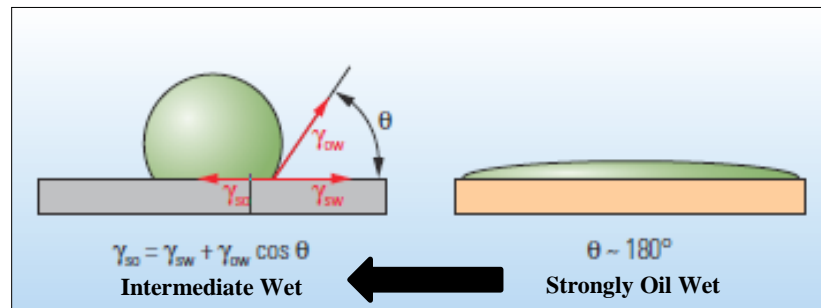


Figure-2: Expected wettability Alteration conditions during immiscible CO₂ flooding process

Similarly, the wettability alteration will behave exponentially as the system got exposed to CO₂ for long time (Figure-3). The contact angle will be dropped from – 1 (strongly oil-wet) to reach almost 0 (intermediate-wet).

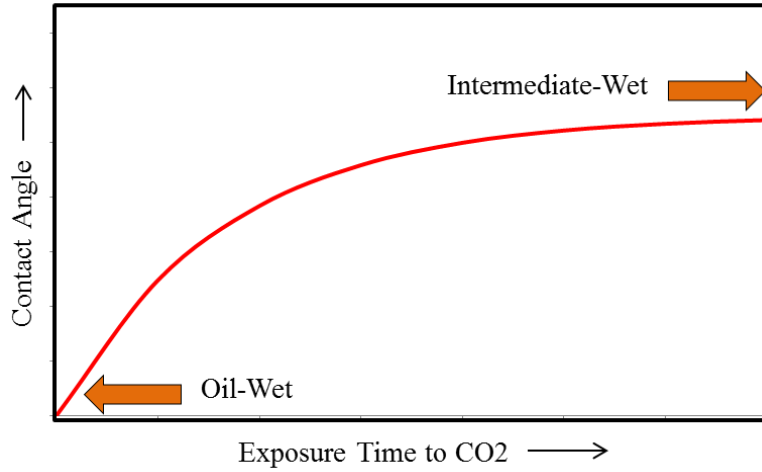


Figure-3: Expected wettability alteration behavior during CO₂ flooding process

Based on the above discussion the relationships of residual oil saturation with contact angle and contact angle with exposure time to CO₂ can be expressed as:

$$S_{or} = ae^{bcos\theta} \quad (4)$$

$$cos\theta = ce^{dt} \quad (5)$$

Respectively.

Coefficients of a & b in equation (4) can be found through the expected boundary conditions as follows:

Initial: Strongly oil wet ($\theta = 180^\circ$):

$$\cos(180^\circ) = -1 \quad (6)$$

Final: Intermediate wet ($\theta = 90^\circ$):

$$\cos(90^\circ) = 0 \quad (7)$$

Substituting equations (6 & 7) into equation (4) yields:

$$(S_{or})_i = ae^{-b} \quad (8)$$

$$a = (S_{or})_f \quad (9)$$

Substituting equation (9) into equation (8) yields:

$$(S_{or})_i = (S_{or})_f e^{-b} \quad (10)$$

Taking \ln for equation (10) yields:

$$b = \ln \left(\frac{(S_{or})_f}{(S_{or})_i} \right) \quad (11)$$

$$S_{or} = (S_{or})_f e^{\ln \left(\frac{(S_{or})_f}{(S_{or})_i} \right) \cos \theta} \quad (12)$$

Re-arranging equation (12) yields:

$$S_{or} = (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos \theta} \quad (12)$$

Substituting equation (13) into equation (1) yields:

$$S_{on} = \frac{S_o - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos \theta}}{1 - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos \theta} - S_{wi}} \quad (14)$$

Substituting equation (14) into equations (2 & 3) yields:

$$k_{ro} = k_{ro}^o \left[\frac{S_o - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos \theta}}{1 - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos \theta} - S_{wi}} \right]^{no} \quad (15)$$

$$k_{rCO_2} = k_{rg}^o \left[1 - \left(\frac{S_o - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos\theta}}{1 - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i} \right)^{\cos\theta} - S_{wi}} \right) \right]^{ng} \quad (16)$$

Corey measured gas (non-wetting phase) relative permeability to estimate the oil (wetting phase) relative permeability. He found that for the high permeability rocks has was examining, no & ng can be at 4 and 2 respectively. Equations (15 & 16) calculate k_{ro} & k_{rCO_2} as function of $\cos\theta$. The other two coefficients (c & d) in equation (5) will be estimated experimentally.

Numerical Simulation Model Description

One dimension model was built utilizing MATLAB software. The objective of this model is to simulate fluid flow displacement of two immiscible phases which are oil and CO₂ gas. A reservoir is assumed that it is surrounded with known geometry and contains oil only. Initial pressure and saturation are uniform throughout the reservoir. The flow is assumed to be linear and parallel to x-axis. The pore space is assumed to be completely filled with oil. CO₂ is injected at one end at constant rate. CO₂ gas will be in gas phase throughout the whole process. Oil and CO₂ velocities are constant (steady state). The injection and production rates of CO₂ and oil are measurable. Initial oil saturation and pressure are known. The flooding is immiscible (no slippage flow and no capillary end effect). The system is compressible and the flow is isothermal. The rock is assumed to be strongly oil-wet initially. Initial immobile water phase is considered.

The new modified relative Corey permeability model derived earlier was incorporated in the model to calculate the oil and gas relative permeability equations (15 & 16). Equation (5) was used in the model to handle the wettability

alteration on continuous basis. The coefficients of coefficients (c & d) was assumed as -1 and -0.06 respectively to represent the expected exponential behavior.

Material balance equations for saturation and pressure were applied in the model to calculate the pressure and gas saturation. IMPES approach was considered in computation process which means that the pressure was calculated implicitly while saturation was calculated explicitly. Figure-4 shows the schematic of the one dimensional model considered in the MATLAB software. The rest input data used in the model is presented in Table-2.

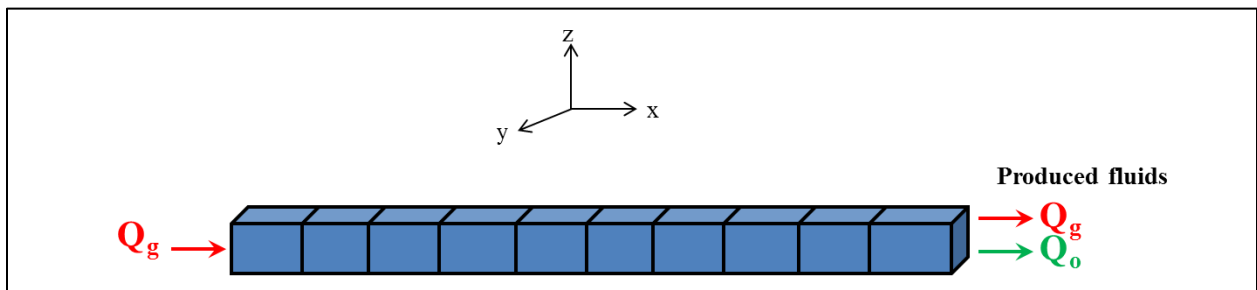


Figure-4: One-dimensional schematic used in MATLAB software

Results and Dissection

Two cases were considered in the numerical simulation model: with and without wettability alteration. Three durations of simulation model were run: 1, 5 and 10 days of CO_2 flooding (figures-5 to 7). It was noticed that the flood front of gas saturation with wettability alteration is always higher. During 1 day of CO_2 flooding, the gas saturation with wettability alteration is slightly higher. During 5 and 10 days of CO_2 flooding, the gas saturation is higher by 5% for the case with wettability alteration. The gap between the two fronts of gas saturation becomes wider as the time of gas exposure gets longer in the model. Incorporating

wettability alteration model shows that the oil recovery can be increased by about 2% (figure-8). The magnitude of wettability alteration will be higher (figure-9). The contact angle was increased to almost -0.75 when the model got exposed to CO_2 for 5 days. The contact angle was increased less to -0.86 and -0.97 when the model got exposed shorter to CO_2 for 2.5 and 0.5 days. Although the flood front did not reach the assumed residual oil saturation limit which is 0.25, the oil relative permeability shifts slightly to the left indicating to a change in wettability condition from strongly oil-wet to the side of intermediate-wet (figure-10). The gas relative permeability is not expected to be changed since the gas has usually no tendency to be a wetting phase.

The above observations can be explained by the mixing occurred between the gas and oil resulting in oil viscosity reduction, swollen oil droplets, interfacial tension reduction and asphaltene precipitation. Since the solubility of CO_2 is higher in oil than in water, the CO_2 changed the oil compositions followed by interactions between the oil compositions and the minerals of rock surface. The adsorption of polar compounds and/or the deposition of organic matter that was originally in the crude oil can alter most of the rock surface mineralogy. The polar compounds contain a polar end and a hydrocarbon end. The polar end adsorbs on the rock surface, exposing the hydrocarbon end and making the surface oil wet (Anderson, 1986). So that, longer exposure of CO_2 to the rock, more interactions will be occurred resulting in higher wettability alteration.

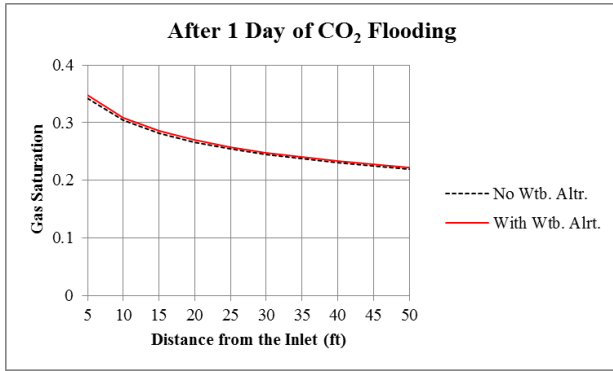


Figure-5: Flood front of gas saturation after 1 day of CO2 flooding

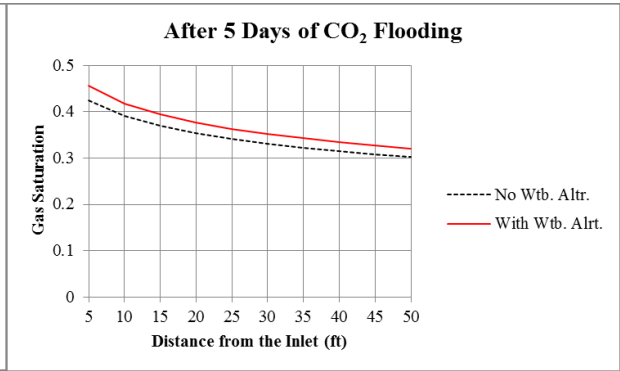


Figure-6: Flood front of gas saturation after 5 days of CO2 flooding

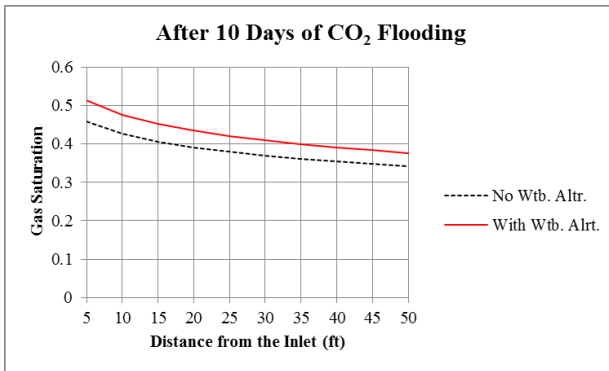


Figure-7: Flood front of gas saturation after 10 days of CO2 flooding

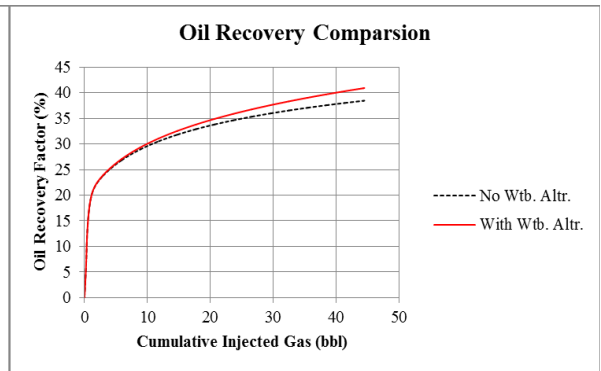


Figure-8: Oil recovery comparison profile

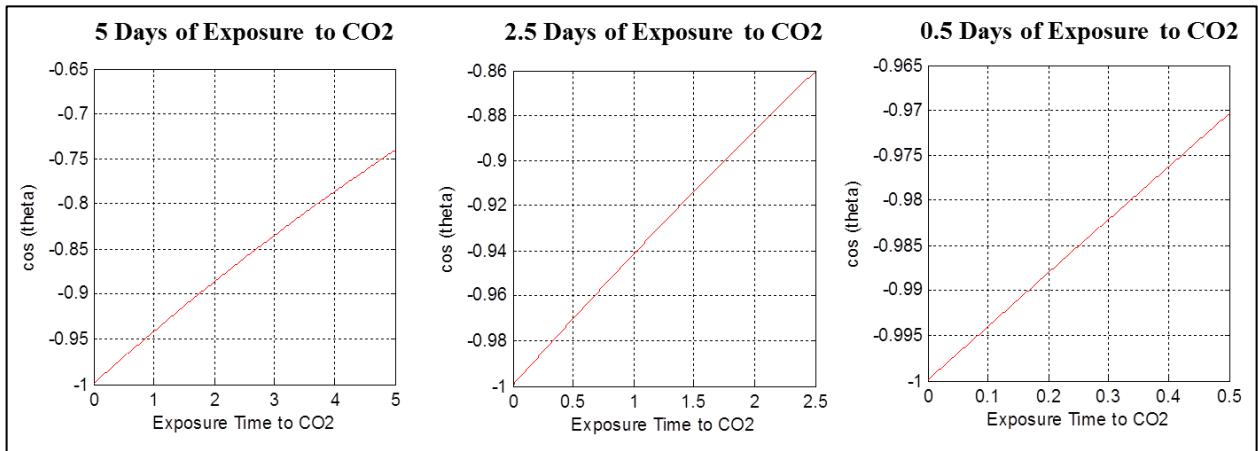


Figure-9: Contact angle response for three different exposure time to CO2 flooding

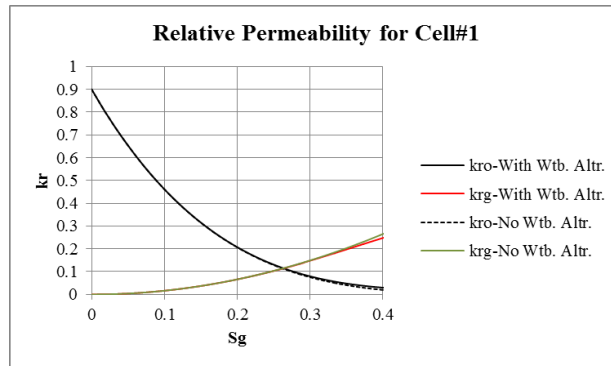


Figure-10: Relative permeability curve

Conclusion

A novel way of determining the Corey relative permeabilities of the oil and CO₂ phases as functions of wettability was developed to handle wettability alteration continuously during CO₂ flooding process. A two-phase immiscible simulation model was built numerically utilizing MATLAB program. This study showed that the inclusion of wettability alteration is very influential parameter in enhancing oil recovery and sweeping the reservoir efficiently. Further investigations will be required to study the wettability alteration during CO₂ flooding process. One of the most important investigations is lab experiments to measure the rate change of contact angle with the exposure time to CO₂. The way of conducting such experiments needs to be designed properly to mimic the expected physics behavior especially if we know that no such experiments were conducted as they are not reported in the literature yet.

Table 1: Comparison of some widely accepted models addressing wettability alterations

| Authors | Model | Remarks |
|-------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Van Dijke and Sorbie (2002) | In water wet pores: $0 \leq \cos \theta_{ow} \leq 1$ In oil-wet pores: $-1 \leq \cos \theta_{ow} < 0$ $P_{c,ij} = \frac{2\sigma_{ij} \cos \theta_{ij}}{r}$ $\cos \theta_{go} = \frac{1}{2\sigma_{go}} \{C_{S,o} \cos \theta_{ow} + C_{S,o} + 2\sigma_{go}\}$ $\cos \theta_{gw} = \frac{1}{2\sigma_{gw}} \{(C_{S,o} + 2\sigma_{ow}) \cos \theta_{ow} + C_{S,o} + 2\sigma_{go}\}$ | 1) Applied Young Laplace equations. 2) Wettability represented through contact angle measurements. 3) Incorporation of double and multiple displacements for mobilization of disconnected phase clusters. 4) Implemented outlet boundary conditions that are consistent with intra-system pressure changes. |
| Delshad et al. (2006) | $k_{rl} = k_{rl}^o \bar{S}_l^{nl} \quad l = 1,2,3$ $\bar{S}_l = \frac{S_l - S_{lr}}{1 - \sum_{l=1}^3 S_{lr}} \quad l = 1,2,3$ $S_{lr} = \min \left[S_l \left(S_l^{high} + \frac{S_{lr}^{low} - S_{lr}^{high}}{1 + T_l N_{Tl}} \right) \right] \quad l = 1,2,3$ $N_{Tl} = \frac{\left -\frac{\partial}{\partial k} \cdot \frac{\partial}{\partial \nabla} \phi_l - \frac{\partial}{\partial k} \cdot \left[g(\rho_{l'} - \rho_l) \cdot \frac{\partial}{\partial \nabla} h \right] \right }{\sigma_{ll'}}$ $k_{rl}^o = k_{rl}^{o^{low}} + \frac{S_{l'r}^{low} - S_{l'r}}{S_{l'r}^{low} - S_{l'r}^{high}} (k_{rl}^{o^{high}} - k_{rl}^{o^{low}}) \quad l = 1,2,3$ $n_l = n_l^{low} + \frac{S_{l'r}^{low} - S_{l'r}}{S_{l'r}^{low} - S_{l'r}^{high}} (n_l^{high} - n_l^{low}) \quad l = 1,2,3$ $k_{rl} = \omega k_{rl}^{final} + (1 - \omega) k_{rl}^{initial} \quad l = 1,2,3$ $P_c = \omega P_c^{final} + (1 - \omega) P_c^{initial}$ | 1) Wettability represented through measuring the changes in relative permeability and capillary pressure. 2) Limited for natural fractured reservoirs. |
| Farhadinia and Delshad (2010) | Matrix: $\tau_{am-f} = \frac{\partial}{\partial t} \left(\frac{\phi S_\alpha}{B\alpha} \right)_m$ Fracture: $\nabla \lambda_{\alpha f} \left(\nabla P_{\alpha f} - \rho_\alpha \frac{g}{g_c} \nabla Z \right) = \frac{\partial}{\partial t} \left(\frac{\phi S_\alpha}{B} \right)_f + q_{\alpha f} + \tau_{am-f}$ $k_{rl} = \omega k_{rl}^{final} + (1 - \omega) k_{rl}^{initial} \quad l = 1,2,3$ $k_{rl} = k_{rl}^o \left(\frac{S_l - S_{lr}}{1 - \sum_{l=1}^3 S_{lr}} \right)^{n_l} \quad l = 1,2,3$ $P_c = \omega P_c^{final} + (1 - \omega) P_c^{initial}$ $P_{clo} = C_{pc} \frac{\sigma_{ol}}{\sigma_{ow}} \left(1 - \frac{S_l - S_{lr}}{1 - \sum_{l=1}^3 S_{lr}} \right)^{E_{pc}} \quad l = 1 \text{ or } 3$ | 1) Limited for natural fractured carbonate reservoirs only. 2) Using surfactants with a dual porosity model. 3) Applied discrete fracture approach. |
| Ju et al. (2010) | $K'_{rwja} = K_{rwj} + \frac{K'_{rwj} - K_{rwj}}{A_{fc}} A_c$ $K'_{roj} = K_{roj} + \frac{K'_{roj} - K_{roj}}{A_{fc}} A_c$ | 1) Wettability represented through measuring the relative permeability. 2) Relative permeability is a function of volume of asphaltene precipitation. |

Table 2: Input data used in the MATLAB software

| Parameter | Value |
|------------------|----------------------------|
| Qgi | 50 ft ³ /day |
| k | 300 md |
| oil viscoity | 0.70 cp |
| gas viscosty | 0.03 cp |
| porosity | 0.2 |
| dx | 5 ft |
| dy | 1.3 ft |
| dz | 1.3 ft |
| Core Length | 50 ft |
| Swi | 0.1 |
| Sgi | 0 |
| Soi | 0.9 |
| Sor | 0.25 |
| Kro @ Swi | 0.9 |
| Krg @ 1-Sor | 0.7 |
| cg | 0.02 psi ⁻¹ |
| cr | 0.000004 psi ⁻¹ |
| co | 0.000015 pai ⁻¹ |

Nomenclature

| | | |
|-----------------|---|--------------------------------------------------------------|
| MMP | = | <i>Minimum Miscible Pressure</i> |
| WAG | = | <i>Water Alternating Gas</i> |
| $USBM$ | = | <i>United States Bureau of Mines</i> |
| σ_{ij} | = | <i>Interfacial Tension, mf^2</i> |
| θ_{ij} | = | <i>Wettability Degree, xx</i> |
| $P_{c,ij}$ | = | <i>Capillary Pressure, psi</i> |
| r | = | <i>Pore Throat Radius, ft</i> |
| $C_{S,o}$ | = | <i>Oil Spreading Coefficient</i> |
| τ_{m-f} | = | <i>Matrix/Fracture Transfer Flow, L^3/t</i> |
| ϕ | = | <i>Porosity, fraction</i> |
| S | = | <i>Saturation, fraction</i> |
| B | = | <i>Formation Volume Factor, $L^3/std L^3$</i> |
| λ | = | <i>Transmissibility</i> |
| P | = | <i>Pressure, $m/L t^2$</i> |
| ρ | = | <i>Fluid Density, m/L^3</i> |
| g | = | <i>Gravitational Acceleration, L/t^2</i> |
| g_c | = | <i>Gravitational Conversion Factor, mL/t^2F</i> |
| q | = | <i>Production/Injection Rate, L^3/t</i> |
| k_r | = | <i>Relative Permeability</i> |
| ω | = | <i>Interpolation Scaling Factor</i> |
| k_r^o | = | <i>Endpoint Relative Permeability</i> |
| C_{pc} | = | <i>Capillary Pressure Endpoint, $m/L t^2$</i> |
| n_l | = | <i>Relative Permeability Exponent</i> |
| T | = | <i>Input Trapping Number</i> |
| N_{Tl} | = | <i>Trapping Number</i> |
| \Rightarrow_k | = | <i>Permeability Tensor, L^2</i> |
| $\nabla \phi_l$ | = | <i>Flow Potential Gradient</i> |
| ϕ_l | = | <i>Potential, $m/L t^2$</i> |

| | | |
|-----------------------|---|--------------------------------------------------------------------------|
| A_{fc} | = | <i>Deposition Volume of Asphaltene Enough to cover all Pore Surfaces</i> |
| A_c | = | <i>Deposition Volume of Asphaltene Coating on Pore Walls</i> |
| K'_{rwja}/K'_{roja} | = | <i>Relative Permeabilities after Asphaltene Deposition</i> |
| K'_{rwj}/K'_{roj} | = | <i>Relative Permeabilities as Asphaltene 100% Occupation</i> |
| K_{rwj}/K_{roj} | = | <i>Relative Permeabilities before Asphaltene Deposition</i> |

Subscripts

| | | |
|-------------|---|-----------------------------|
| ij | = | <i>ow, gw, go</i> |
| α | = | <i>Phase</i> |
| m | = | <i>Matrix</i> |
| f | = | <i>Fracture</i> |
| l | = | <i>Water</i> |
| r | = | <i>Residual</i> |
| <i>high</i> | = | <i>High Trapping Number</i> |
| <i>low</i> | = | <i>Low Trapping Number</i> |

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