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A Novel Approach to Handle Continuous Wettability Alteration during Immiscible CO_2 Flooding Process

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Abstract

Wettability has been recognized as one of the main parameters that control the remaining oil-in-place. Knowledge of wettability alteration during displacement 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 enhanced oil recovery (EOR). Review of the literature reveals that much laboratory work, including core and micro-model flooding, was conducted to investigate wettability alteration during CO_2 flooding process. However, limited research on numerical and/or analytical modeling of such wettability alteration has been reported. Moreover, to the best of our knowledge, published numerical and/or analytical models are time-independent solutions. Ignoring this time dimension creates a significant knowledge gap between such solutions and reality. To mitigate this shortcoming, a novel approach was developed to handle wettability alteration on continuous basis during immiscible CO_2 flooding process.

A mathematical model was developed to incorporate continuous time function for immiscible CO_2 flooding process. During the development of the model equation, Cory relative permeability model was utilized. In this model, a new, modified Corey relative permeability model was incorporated to calculate the phase relative permeability as a function of wettability. A numerical, 1-dimensional, two-phase immiscible simulation scheme was built utilizing MATLAB program to solve the model equations. The results showed that inclusion of continuous wettability alteration model is believed to predict oil displacement and sweep efficiency more realistically.

Introduction

Wettability alteration is an effective approach to enhance oil recovery significantly. Buckley et al., (1998) summarized four main factors affecting wettability alteration which are: oil composition, brine chemistry, rock surface mineralogy and the system temperature, pressure and saturation history. The adsorption and the deposition of organic polar components in the crude oil can alter most of the rock surface chemistry. Brine salinity and pH strongly affect the charge of the rock surface where the rock surface becomes positively charged when the pH is decreased and the opposite is true. The solubility of wettability-altering compounds tends to increase when both temperature and pressure are elevated.

In an oil-bearing formation, the wettability can vary with depth, where a greater water-wetting preference is encountered near the bottom of the transition zone and a greater oil-wetting preference is seen 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 (Boyd et al., 2007).

Wettability alteration during CO_2 flooding has been investigated extensively in the literature through core-flooding experiments (Stalkup, 1970; Tiffin and Yellig, 1983; Maini et al., 1986; Potter, 1987; Lin and Huang, 1990; Rao et al., 1992; Vives et al., 1999; Zekri et al., 2007; Fjelde and Asen, 2010), and investigators have proved experimentally that wettability can be altered as a result of CO_2 injection. On the other hand, a limited number of modeling studies on wettability alteration during CO_2 displacement is documented in the literature (Tehrani et al., 2001; van Dijke and Sorbie, 2002; Farhadinia and

Delshad, 2010; Ju et al., 2010; Kalaei et al., 2012). However, the published studies have numerous limitations in their modeling and solution parts. One such limitation is the solutions presented by the published numerical/analytical models are time-independent where 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 was totally absent in the solutions of these models. This shortcoming creates a significant knowledge gap between the analytical/numerical solution and reality. Therefore, bridging this gab through development of a time-dependent model to trace the wettability alteration during CO_2 flooding process is very useful. This work reveals the importance of including wettability alteration in modeling such a process. A novel way was developed to calculate the relative permeability of oil and CO_2 as a function of contact angle.

Contact Angle Model Development

Starting with an oil-wet porous medium fully saturated with water and residual oil; and if we expose the system to CO_2 gas, the wettability is expected to gradually change from oil-wet to intermediate-wet as CO_2 diffuses through the water to the rock surface. The contact angle would then be expected to decrease exponentially with CO_2 exposure time as conceptually depicted in Figure 1 as well as experimentally established (Mutairi et al., 2012). However, such decrease would approach a certain limit asymptotically as the contact angle cannot go below zero.

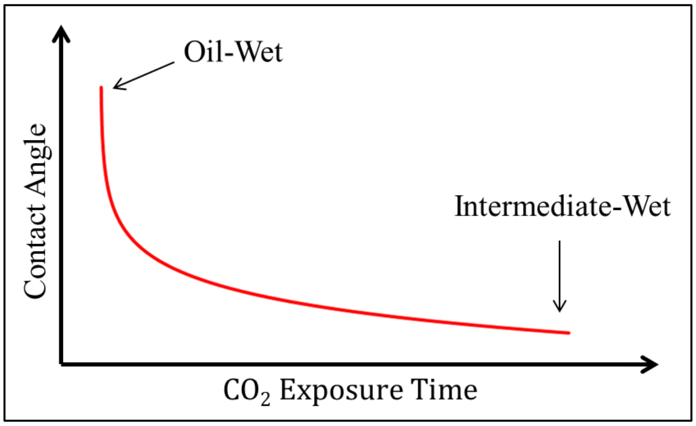

Figure 1: Contact angle variation with CO_2 exposure time

Based on the above concept, the relationship between the contact angle and CO_2 exposure time can be modeled as follows:

$$\theta = ae^{-bt} + c \tag{1}$$

In Eq. (1) $\boldsymbol{a, b\ and\ c}$ are coefficients related to rock and fluid compositions as well as aging history and process parameters. These coefficients were estimated experimentally as presented below.

A carbonate core plug was saturated with dead oil at a known immobile brine saturation using a core flooding setup. Properties of the rock and fluids employed in the experiment are presented in Tables 1 and 2. After aging, the surface of the core slice was then grinded to a uniform shape to allow accurate measurement of the contact angle. The core slice was then attached to the hanger using special epoxy cement which has high resistance to temperature (Figure 2). The hanger was then mounted inside the visual cell. The cell was then filled completely with brine and heated to 70 ºC and pressurized to 500 psig. A drop of the dead oil was then introduced to the cell through a vertical needle fitted to the bottom of the cell. The needle is positioned directly below the core slice so that when the drop enters the cell it rises through the brine and rests on the lower surface of the core slice (Figure 3). The contact angle between the oil drop and the surrounding brine was then measured.

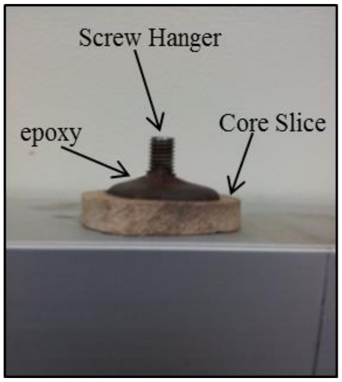

Figure 2: Core slice-hanger assembly

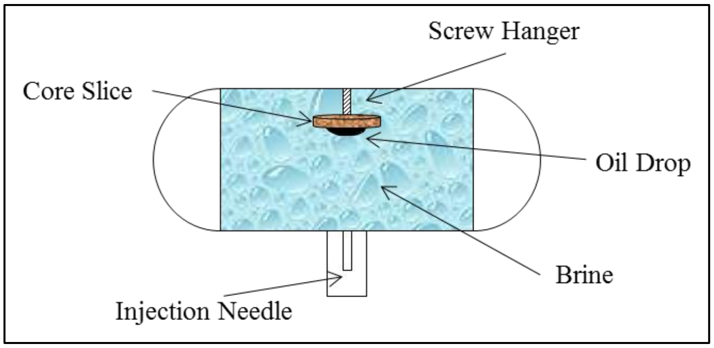

Figure 3: Visual cell components

Table 1: Properties of the rock and fluids employed in the experiment

Property	Value
Oil density (g/cc)	0.85
Oil viscosity (cP)	0.71
Brine density (g/cc)	0.99
Brine viscosity (cP)	0.56
Core permeability (mD)	100
Core porosity (%)	15

Table 2: Brine composition

Salt	Concentration g/L
Sodium Chloride (NaCl)	16.7
Calcium Chloride ($CaCl_2.2H_2O$)	3.62
Magnesium Chloride ($MgCl_2.6H_2O$)	1.28

CO_2 gas (99.5% pure with moisture content less than 120 ppm) was then rapidly charged to the cell until the cell's pressure rose to a pre-determined level (about 1000 psig); CO_2 injection was then stopped. When the cell's pressure dropped back to 500 psig, which usually took about 15 seconds, indicating complete dissolution of CO_2 in the brine, high-resolution photographs of the oil drop were then taken periodically until no noticeable change in the shape of the drop was observed. The photographs were then analyzed and values of the contact angle versus the drop's exposure time to the carbonated brine were recorded.

The experiment was conducted at brine CO_2 concentrations of 0.0008 mole percent. The CO_2 concentration was calculated by volumetric balance on the cell's contents. Table 3 lists the results of the experiment, which are also plotted in Figure 4.

Table 3: Variation contact angle with time

CO_2 Exposure Time (Minute)	Contact Angle (Degree)
0	97.5
17	74.8
23	72.8
25	72.8
28	73
32	73
34	69.2
36	69.1
39	69.4
44	69.4
52	69.3
76	69.3
83	69.3
89	69.3

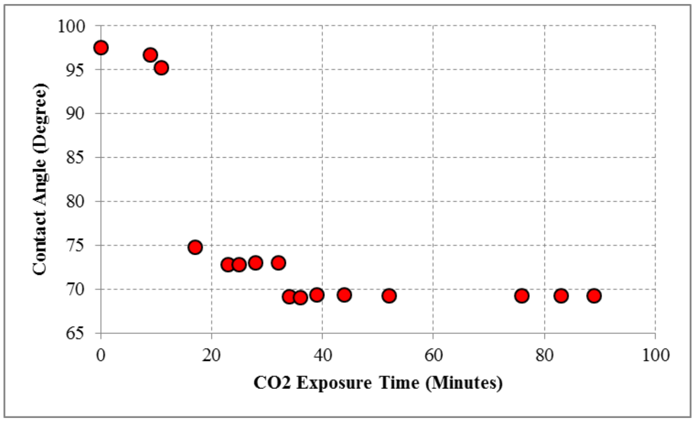

Figure 4: Raw experimental data

The results demonstrate that the rock wettability was altered when the rock was exposed to CO_2. The contact angle decreased from 97.5º initially to reach a stable value of about 69.3º after 52 minutes of exposure to the carbonated brine. The initial decrease in the angle was rapid followed by a gentle trend towards a stable value. The change in contact angle shows that the wettability of the core slice was altered from slightly oil-wet to intermediate-wet. When the exposure time was extended to 89 minutes no change was observed in the angle confirming the existence of a stable value. The trend of the data reveals an asymptotic-exponential relationship between the contact angle and exposure time.

The coefficients of the model equation (1) were determined by non-linear regression (Figure 5) to be:

$$\theta = 28e^{-0.09t} + 69 \qquad (2)$$

Where $a = 28$, $b = 0.09$, and $c = 69$.

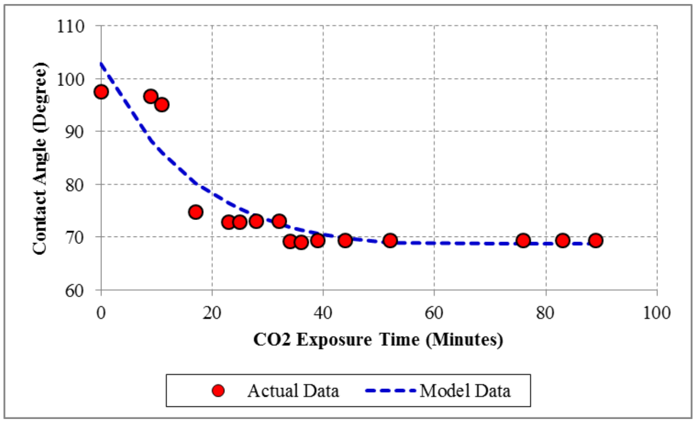

Figure 5: Raw experimental data with fitting curve

New Modified Corey Relative Permeability Model

Core flooding experiments showed that the maximum oil recovery apparently occurs in neutral or slightly oil-wet cores (Morrow and Mungan, 1971; Lorenz et al., 1974). Strong oil wettability results in low oil recovery because the wetting phase (oil) occupies the small pores, which leads to a high residual oil saturations. In contrast, the residual oil saturation in intermediate-wet rocks decreases if water shares those small pores. Therefore, it is theoretically plausible to speculate that the residual oil saturation will follow an exponential relationship with the rock wettability as depicted in Figure 6.

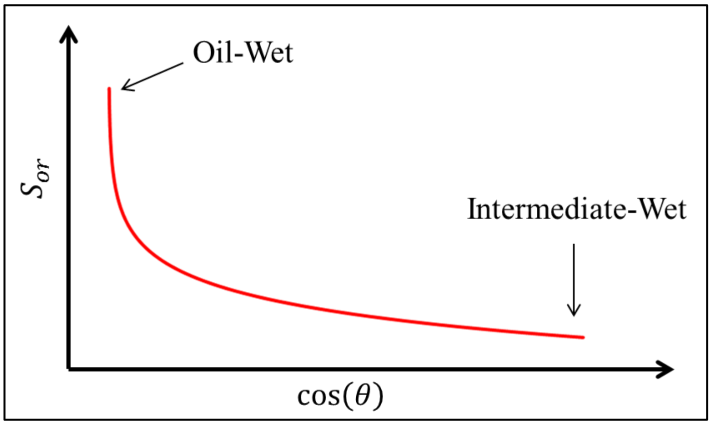

Figure 6: Residual oil saturation variation with contact angle

Therefore, the relationship between the resduial oil saturation and the rock wettability can be represented by:

$$S_{or} = de^{g\cos\theta} \quad (3)$$

Phase relative permeability relationship is a vital parameter in assessing the recovery efficiency for a particular reservoir. Normalized phase saturation is a well-established representation of phase relative permeability and can be expressed as (Koedertiz et al., 1989):

$$S_{on} = \frac{(S_o - S_{or})}{(1 - S_{or} - S_{wi})} \quad (4)$$

Corey (1954) introduced the power law model that is often called the "Corey model" to represent relative permeability of oil and gas as follows:

$$k_{ro} = k_{ro}^{o} S_{on}^{no} \quad (5)$$

$$k_{rCO_2} = k^{o}_{rCO_2}(1 - S_{on})^{ng} \tag{6}$$

Constants d & g in Eq. (3) can be determined from the following assumed boundary conditions:

Initial condition: strongly oil-wet ($\theta = 180^{\circ}$):

$$\cos(180^{\circ}) = -1 \tag{7}$$

Final condition: intermediate-wet ($\theta = 90^{\circ}$):

$$\cos(90^{\circ}) = 0 \tag{8}$$

Substituting Eqs. (7 & 8) into Eq. (3):

$$(S_{or})_i = de^{-g} \tag{9}$$

$$d = \ (S_{or})_f \tag{10}$$

Substituting Eq. (10) into Eq. (9):

$$(S_{or})_i = (S_{or})_f e^{-g} \tag{11}$$

Taking log_e of both sides of Eq. (11):

$$g = \log_e\left(\frac{(S_{or})_f}{(S_{or})_i}\right) \tag{12}$$

Substitiuting d & g into Eq. (3) yields:

$$S_{or} = (S_{or})_f e^{\log_e\left(\frac{(S_{or})_f}{(S_{or})_i}\right) cos\theta} \tag{13}$$

Re-arranging Eq. (13) yeilds:

$$S_{or} = (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta} \tag{14}$$

Substituting Eq. (14) into Eq. (4):

$$S_{on} = \frac{S_o - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta}}{1 - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta} - S_{wi}} \tag{15}$$

Substituting Eq. (15) into Eqs. (5 & 6):

$$k_{ro} = k^{o}_{ro}\left[\frac{S_o - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta}}{1 - (S_{or})_f \left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta} - S_{wi}}\right]^{no} \tag{16}$$

$$k_{rCO_2} = k_{rCO_2}^{o}\left[1-\left(\frac{S_o-(S_{or})_f\left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta}}{1-(S_{or})_f\left(\frac{(S_{or})_f}{(S_{or})_i}\right)^{cos\theta}-S_{wi}}\right)\right]^{ng} \tag{17}$$

Equations (16 & 17) represent k_{ro} & k_{rCO_2} as functions of rock wettability. If the variation of the contact angle with time – such as given by Eq. (1) – is introduced into Eqs. (16 & 17), then these equations can track the wettability alteration of an oil-wet medium undergoing immicible displacement by CO_2. The relative permeability to oil decreases with reduction of the contact angle indicating that oil becomes confined to the smallest pores as the medium is altered from oil wet to intermediate wet. On the other hand, CO_2 relative permeability increases as both the gas and aqueous phases invade the medium-sized pores occupied originally by oil. CO_2 does not enter the small pores since gases usually have no tendency to be the wetting phase (Egermann et al., 2006). Corey measured gas (non-wetting phase) relative permeability to estimate the oil (wetting phase) relative permeability and found that no and ng can be 4 and 2, respectively, for high permeability rocks (Corey 1954).

Numerical Simulation Model Description

MATLAB programming was used to solve Eqs. (16 & 17) for a 1-D, Cartesian coordinate system (Figure 7). The objective was to simulate immiscible displacement of oil by CO_2 gas. A strongly-oil wet porous medium containing oil was considered where compressible, isothermal and steady-state flow conditions prevail for all phases. The initial pressure and saturations are uniform throughout the medium and the volumetric flow is linear parallel to x-axis. The small pores are assumed to be completely filled with oil. CO_2 is injected at one end at a constant rate and remains in the gaseous state throughout the displacement process. An initially immobile water phase is also included.

The new modified Corey relative permeability model derived earlier [Eqs. (16 & 17)] was incorporated in the simulator to calculate the oil and gas relative permeabilities. Equation (2) was used in the model to handle the wettability alteration on continuous basis. Material balance equations for saturation and pressure were applied in the model to calculate the pressure and saturation in each grid cell. The Implicit Pressure Explicit Saturation (IMPES) approach was considered in the computation scheme, which means that the pressure was calculated implicitly while saturation was calculated explicitly. The pressure equation in the IMPES scheme is obtained after summation of Darcy's laws and substituting them into the summation of the two mass conservation equations for each phase (Negara, 2011). Gas saturation (S_{CO_2}) is then calculated after obtaining pressure of each grid cell. The rest of input data used in the model is presented in Table 4.

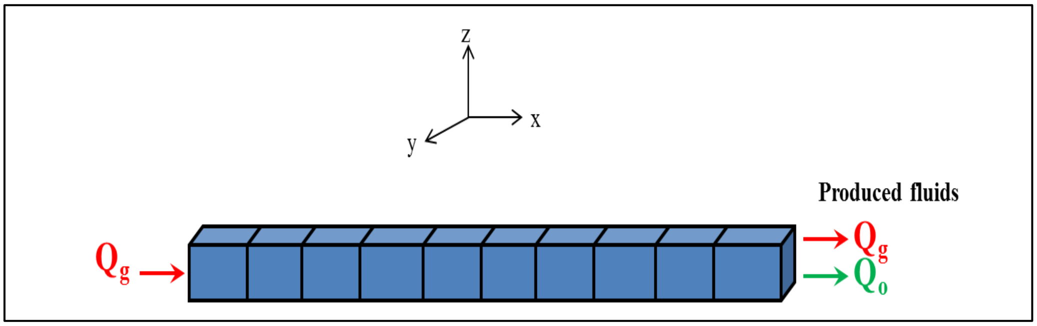

Figure- 7: Schematic of the one-dimensional flow system

Table 4: Input data for the simulation model

Parameter	Value
Q_{gi}	50 ft^3/day
k	100 mD
oil viscosity	0.70 cP
gas viscosity	0.03 cP
porosity	0.15
Δx	5 ft
Δy	1.3 ft
Δz	1.3 ft
Medium’s Length	50 ft
S_{wi}	0.1
S_{gi}	0
S_{oi}	0.9
S_{or}	0.25
k_{ro} @ S_{wi}	0.9
k_{rg} @ 1-S_{or}	0.7
c_g	0.02 psi^{-1}
c_r	0.000004 psi^{-1}
c_o	0.000015 psi^{-1}

Results and Discussion

Two cases were considered in the numerical simulation model: with wettability alteration and without. Two CO_2 flooding durations were investigated: 1 and 10 days (Figure 8). It is noticed that the gas saturation profile is higher when wettability alteration is assumed suggesting more oil is displaced. After 1 day of CO_2 flooding, the gas saturation with wettability alteration is higher than the case with no wettability alteration by about 12%; after 10 it is higher by almost 15%. The gap between the two profiles becomes wider as the flooding time is extended. Incorporating the wettability alteration model shows that the predicted oil recovery is about 13% higher at 4 PV’s of CO_2 injection (Figure 9), and this gap in recovery is destined to be larger with continued CO_2 injection. The largest reduction in the contact angle is observed in cell#1 (to almost 96.57°) since this cell has been exposed to CO_2 for the longest time (Figure 10). The reduction in the contact angle decreases as we move away from the injection end as is the case with cell#5 and cell#10. Figure 11 shows the relative permeability curves with and without wettability alteration. The crossover point is shifted to the right from Sg = 0.27 to 0.37. The trend in relative permeability curves shows these curves stretching over a wider range of gas saturation. This is obviously caused by oil displacement from medium size pores. It could also be attributed to re-distribution of the water phase. As the wettability is altered from oil wet to intermediate wet, the dispersed water drops that were restricted to large pores can now invade medium pores and, thus, vacate the large pores to the gas phase.

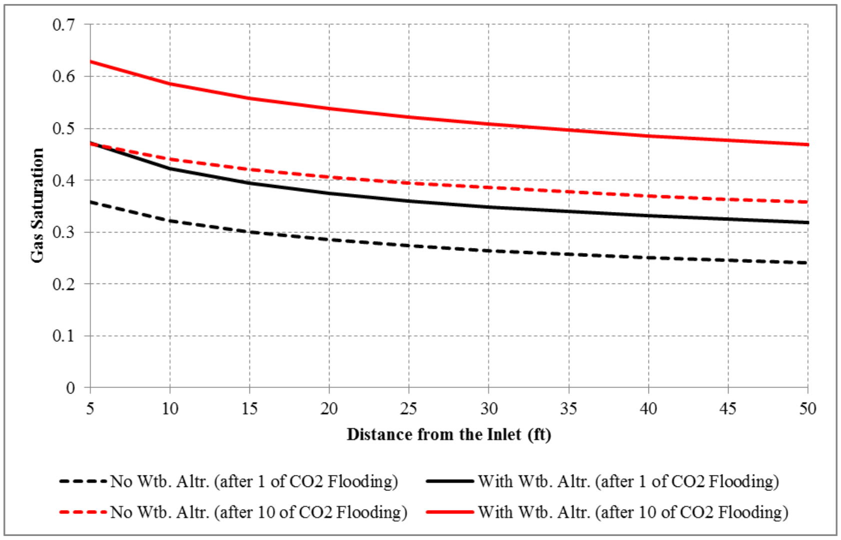

Figure- 8: Gas saturation profiles after 1 & 10 days of CO_2 flooding

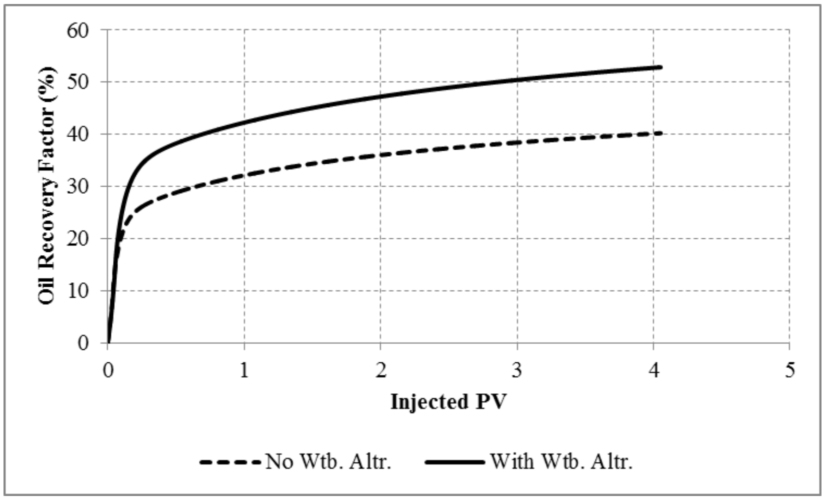

Figure- 9: Oil recovery comparison

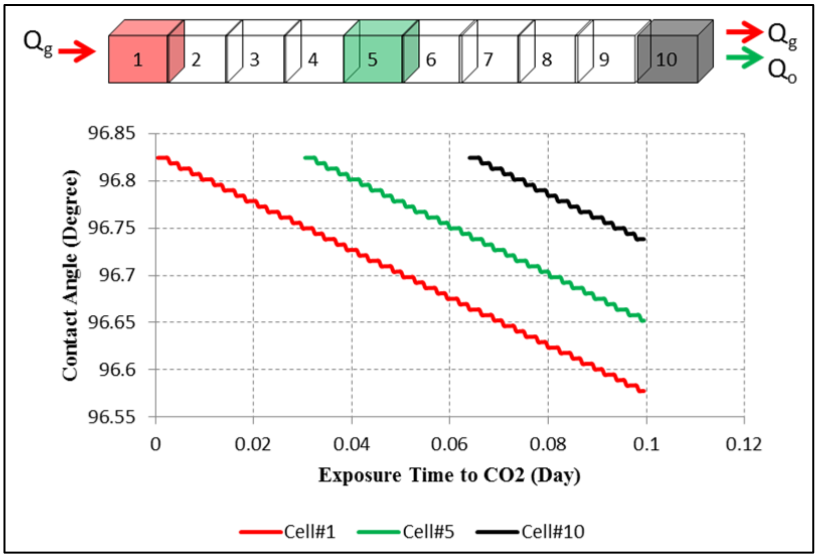

Figure- 10: Contact angle variation for three different cells

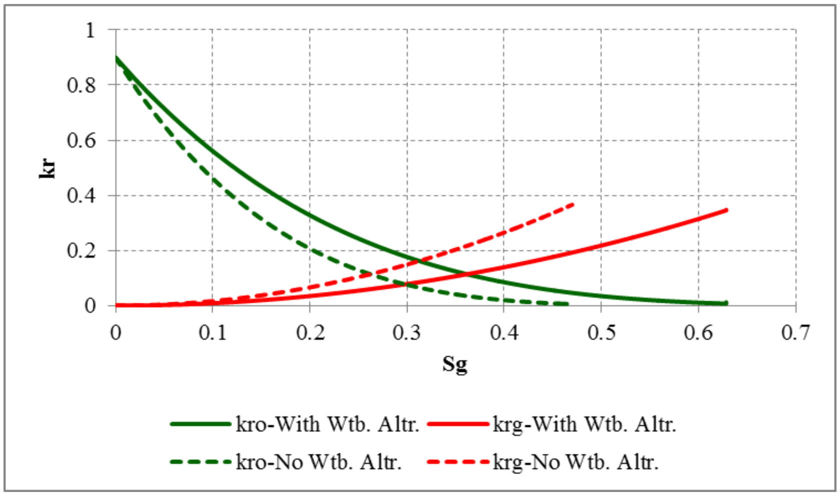

Figure- 11: Relative permeability curves

Conclusions

A novel way of determining the Corey relative permeabilities of the oil and CO_2 phases as functions of wettability was developed to handle wettability alteration continuously during immscible CO_2 flooding process. Measurements of the contact angle between oil, carbonated brine and a slice of rock cut from a carbonate core plug were conducted. The experimental results indicate that the rock wettability is altered from oil-wet to intermediate-wet when the oil/rock system is exposed to dissolved CO_2. The results show that inclusion of wettability alteration predicts a significantly larger oil displacement.

Nomenclatures

k_{ro} = oil relative permeability
k_{rCO_2} = CO_2 relative permeability
k_{ro}^{o} = oil relative permeability (at $S_g = 0$)
$k_{rCO_2}^{o}$ = CO_2 relative permeability (at $S_g = 1 - S_{or}$)
S_{or} = resdiual oil saturation
$(S_{or})_i$ = initial resdiual oil saturaiton
$(S_{or})_f$ = final resdiual oil saturaiton
S_o = oil saturation
S_{wi} = initial water saturation

S_{on} = normalized oil saturation
no = oil phase Corey exponent
ng = gas phase Coery exponent
θ = contact angle in degrees
t = CO_2 exposure time in minutes

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