

# Simulation Study of Asphaltene Deposition and Solubility of CO<sub>2</sub> in the Brine during Cyclic CO<sub>2</sub> Injection Process in Unconventional Tight Reservoirs

Rashid S. Mohammad, Shicheng Zhang, Sun Lu, Syed Jamal-Ud-Din, Xinzhe Zhao

**Abstract**—A compositional reservoir simulation model (CMG-GEM) was used for cyclic CO<sub>2</sub> injection process in unconventional tight reservoir. Cyclic CO<sub>2</sub> injection is an enhanced oil recovery process consisting of injection, shut-in, and production. The study of cyclic CO<sub>2</sub> injection and hydrocarbon recovery in ultra-low permeability reservoirs is mainly a function of rock, fluid, and operational parameters. CMG-GEM was used to study several design parameters of cyclic CO<sub>2</sub> injection process to distinguish the parameters with maximum effect on the oil recovery and to comprehend the behavior of cyclic CO<sub>2</sub> injection in tight reservoir. On the other hand, permeability reduction induced by asphaltene precipitation is one of the major issues in the oil industry due to its plugging onto the porous media which reduces the oil productivity. In addition to asphaltene deposition, solubility of CO<sub>2</sub> in the aquifer is one of the safest and permanent trapping techniques when considering CO<sub>2</sub> storage mechanisms in geological formations. However, the effects of the above uncertain parameters on the process of CO<sub>2</sub> enhanced oil recovery have not been understood systematically. Hence, it is absolutely necessary to study the most significant parameters which dominate the process. The main objective of this study is to improve techniques for designing cyclic CO<sub>2</sub> injection process while considering the effects of asphaltene deposition and solubility of CO<sub>2</sub> in the brine in order to prevent asphaltene precipitation, minimize CO<sub>2</sub> emission, optimize cyclic CO<sub>2</sub> injection, and maximize oil production.

**Keywords**—Tight reservoirs, cyclic O<sub>2</sub> injection, asphaltene, solubility, reservoir simulation.

## I. INTRODUCTION

THE consumption of petroleum hydrocarbons worldwide has been gradually increasing. Oil production from the unconventional reservoirs is one of the key energy resources that can meet the growing demand of the world's energy. Exploration and production of unconventional reservoirs has attracted attentions since it is available in large quantities worldwide. Tight reservoirs are resources that contain hydrocarbons in extremely low permeable type formations that are inefficient to produce at economical rates with the application of conventional approaches [1]. Therefore, the advanced horizontal drilling and multiple hydraulic fracturing

are commonly used to penetrate unconventional resources such as tight oil, shale gas, and coalbed methane; those resources become very essential to provide enough hydrocarbon to balance the shortage of conventional resources.

The average daily oil production in the U.S. (90% from the unconventional Bakken) was 977,000 barrels from 10,457 producing wells [2]. Hence, each well approximately produces around 95 bbl./day as shown in Fig. 1. The oil production from unconventional reservoirs drops very rapidly around 75% within the first two years in the life of the well; due to the lack of connections between pores, which makes it very challenging to improve it further. However, the primary recovery of unconventional reservoirs remains low to only 8% of the initial oil in place, even though long horizontal wells have been drilled and massively fractured [3].

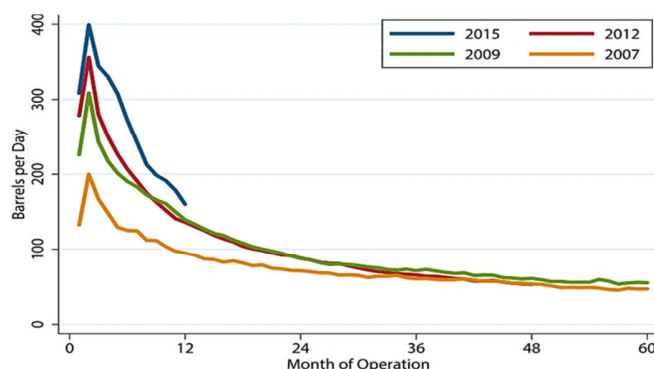


Fig. 1 Primary production of unconventional reservoirs in U. S. [4]

Waterflooding is the most commonly used secondary oil recovery technique in conventional reservoirs, but it is not a feasible choice in ultra-low permeability reservoirs, mainly due to the extremely low injectivity, clay swelling, and poor sweep efficiency issues [5]. Recent studies have shown that gas injection may be a good choice. The reasons for initiating these studies include shortage of efficient and economic techniques for improving oil recovery in tight reservoirs, inefficiency of conventional methodologies such as waterflooding, and the unique nature of unconventional reservoirs like ultra-low porosity and permeability [6]. On the other hand, CO<sub>2</sub> is usually injected for unlocking tight oil formations. Cyclic CO<sub>2</sub> injection process is found to have achieved a good recovery performance in unconventional reservoirs and a promising EOR technique that could overcome some major problems associated with continuous CO<sub>2</sub> flooding, such as early CO<sub>2</sub> breakthrough, high

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operation costs, demand for CO<sub>2</sub> source, etc. Thus, it is essentially important to evaluate performance of cyclic CO<sub>2</sub> injection process, which can diminish early CO<sub>2</sub> breakthrough with the produced fluid. The earlier studies showed the necessity for optimizing cyclic CO<sub>2</sub> injection process. Gamadi et al. [7] performed an experimental work for shale oil reservoir and found that cyclic CO<sub>2</sub> injection process is capable of recovering oil from unconventional shale oil reservoirs. Likewise, Chen et al. [8] evaluated the effect of reservoir heterogeneity on the CO<sub>2</sub> huff-n-puff recovery in a shale matrix using numerical simulation and the ability of CO<sub>2</sub> to penetrate near-fractured regions. Similarly, Song and Yang [9] conducted experimental work as well as numerical simulation to assess the performance of immiscible and miscible cyclic CO<sub>2</sub> injection process in shale formations. However, it is important to study the most significant parameters dominating the CO<sub>2</sub> injection process.

The application of CO<sub>2</sub> to enhance oil recovery can induce asphaltene precipitation which counts as one of the major issue in the oil industry due to its plugging onto the porous media, which reduces the oil productivity. To avoid asphaltene precipitation, reservoir bottom-hole pressure must be greater than the precipitation onset pressure. However, cyclic CO<sub>2</sub> injection process has provided enough support for pressure maintenance, which helps in avoiding asphaltene precipitation [10]. Hamouda et al. [11] reported that, at high CO<sub>2</sub> concentration, asphaltene dissolved in oil begins to flocculate below the onset pressure because the injected CO<sub>2</sub> dissolves in oil, leading to oil swelling and viscosity reduction, thus isolating the light hydrocarbon fractions from the oil and prompting flocculation. Furthermore, Al-Qasim [10] studied asphaltene precipitation, flocculation, and deposition during CO<sub>2</sub> flooding for conventional reservoirs. Leontaritis and Mansoori [12] stated that one main issue during CO<sub>2</sub> injection is asphaltene uncertainty, which induces precipitation and may cause pore-throat-plugging or wettability alteration. Okwen [13] and Srivastava et al. [14] concluded that the presence of water can reduce the asphaltene precipitation. Therefore, it is necessary to have a demonstrative reservoir simulation model that can anticipate the phase behavior of asphaltene deposition precisely.

Global warming and climate change is caused by CO<sub>2</sub> emission, mainly from the combustion of fossil fuels. Thus, solubility of CO<sub>2</sub> in the aqueous phase is one of the safest trapping techniques while considering the CO<sub>2</sub> storage mechanisms in the geological formations. However, dissolution of CO<sub>2</sub> depends on pressure of the system, pressure buildup during injection process could possibly produce or initiate fractures, providing migration pathways for CO<sub>2</sub> that requires safety of storage [15], [16]. Most of researchers are motivated by rising attention in CO<sub>2</sub> sequestration in deep brine aquifers and CO<sub>2</sub> enhanced oil recovery (EOR). Trapping CO<sub>2</sub> in brine aquifers is observed as one of the best applicable technique to reduce CO<sub>2</sub> emission although it is mainly aimed at enhancing oil recovery and controls depletion mechanisms of oil reservoirs. Furthermore, it is observed as an economically feasible technique for underground CO<sub>2</sub> storage. Brine aquifer

mainly consists of NaCl which is considered as the major component of many formation brines. Therefore, many studies have been conducted on the solubility of CO<sub>2</sub> in NaCl brines, which are basically a binary mixture of distilled water and NaCl. Drummond [17] measured more than 500 data points of CO<sub>2</sub> solubility in NaCl brines of different salinities. However, CO<sub>2</sub> solubility is an important concern for CO<sub>2</sub> EOR since CO<sub>2</sub> is much more soluble in the oil than other gas components [18]. Therefore, CO<sub>2</sub> must be taken into account in design and simulation of a CO<sub>2</sub> EOR process.

This study assists in better understanding the behavior of cyclic CO<sub>2</sub> injection process in tight reservoirs while considering the effects of asphaltene deposition and CO<sub>2</sub> solubility. A numerical reservoir simulation model has been generated to evaluate some parameters of the cyclic CO<sub>2</sub> injection scheme, in order to improve techniques for designing cyclic injection treatments [19].

## II. RESERVOIR MODELING APPROACH

Reservoir simulation is an expensive and usually ideal method to assess the concern of such complex formations due to low permeability of tight reservoir. The complex nature of pre-existing natural fractures and their network with hydraulic fractures are combined with horizontal well completion. Numerical simulation performances are commonly recognized in the petroleum industry [1]. Therefore, such tools are considered being fast and simple, which are supportive in making decision for unconventional wells.

The reservoir simulation work for the application of cyclic CO<sub>2</sub> injection process was studied using compositional simulator in Computer Modeling Group CMG-GEM. The dimensions of the reservoir were 2800, 1700, and 20 ft in the x, y and z-directions, respectively. The tight reservoir is stimulated; in this simulation work, only a single half-fractured region was simulated on the basis of flow symmetry and having the dimensions of 300, 800, and 20 ft in the x, y and z-directions, respectively as shown in Fig. 2. However, it can save lots of gridblocks, computation complexities, and time without sacrificing the computing accuracy [20].

### A. Fluid Properties

Phase behavior simulator is depending on the compositional data of the fluid samples, injected fluid and on reservoir pressure and temperature. Reservoir fluid properties provide the main input for any simulator used to predict thermodynamic properties of the fluid based on some reliable data provided by the operating company. Therefore, accurate PVT properties are required to get appropriate and representative simulation results. CMG-WinProp was used for generating fluid model. The fluid sample was taken at an 8500-ft depth. Reservoir initial pressure, temperature, and saturation pressure (bubble Point) at reservoir temperature were 5820 psi, 238 °F and 2652 psi, respectively. Phase behavior simulation showed that first-contact miscibility between the reservoir fluid and CO<sub>2</sub> is first established at 3375 psi, while the multi-contact miscibility occurs at 3125 psi. CO<sub>2</sub> diffusion is a critical factor in CO<sub>2</sub> EOR and its diffusion coefficient between component is calculated

by Sigmund, 1976 [21]:

$$D_{ij} = \frac{\rho_\ell^0 D_\ell^0}{\rho_\ell} (0.99589 + 0.096016 \rho_{\ell r} + 0.22035 \rho_{\ell r}^2 + 0.032874 \rho_{\ell r}^3) \quad (1)$$

where  $\rho_\ell^0 D_\ell^0$  is the product of density and diffusivity at zero pressure,  $\rho_\ell$  is the density of the  $\ell$  phase and  $\rho_{\ell r}$  is the reduced density.

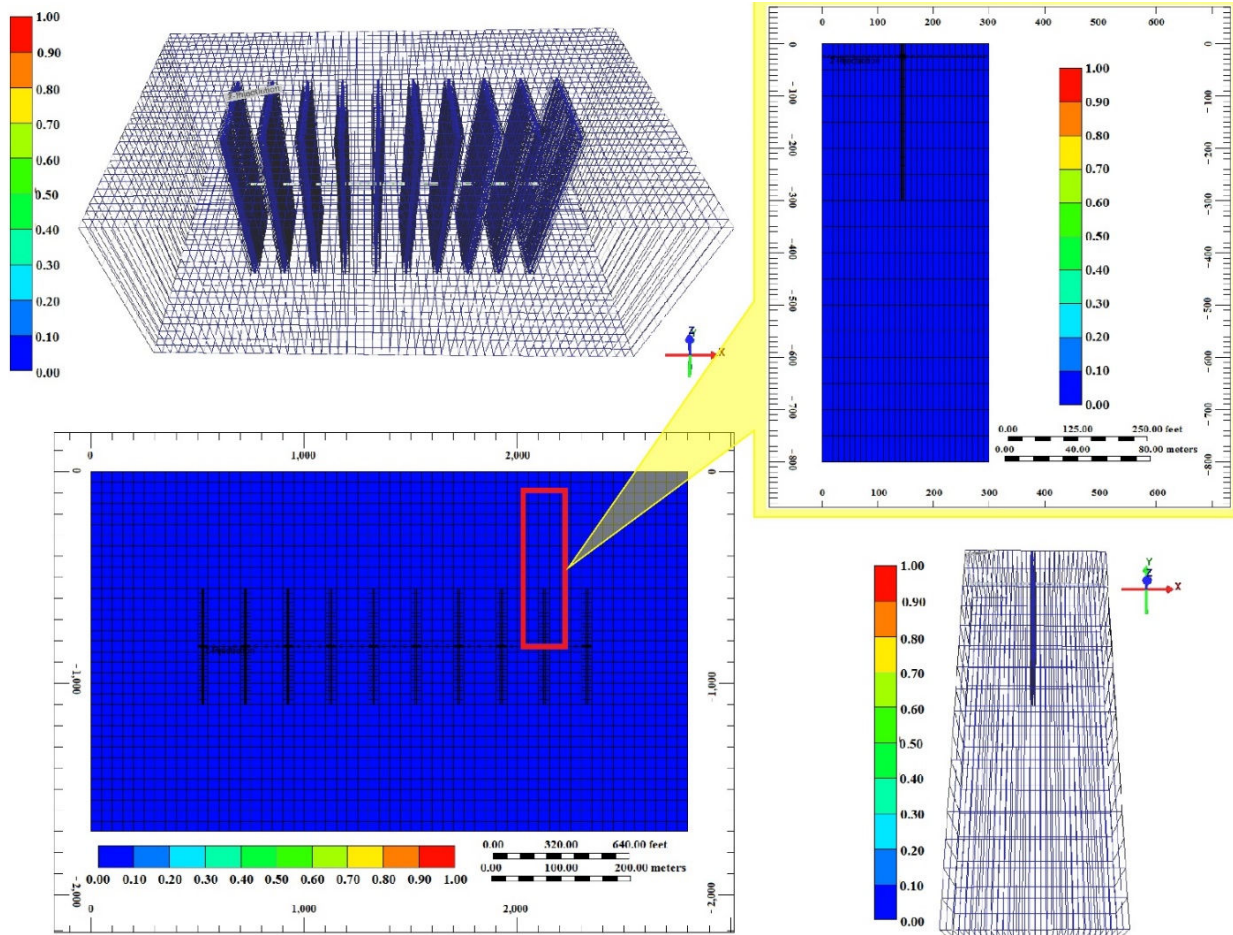


Fig. 2 Stimulated reservoir with 10-hydraulic fractures having 200-ft fracture spacing and 250-ft half-fracture length

The modified Peng-Robinson (1978) equation of state was used, and the critical properties of the heaviest component together with the binary interaction parameter were tuned using regression settings to fit the fluid properties at initial reservoir conditions [22]. Used Peng-Robinson EOS is:

$$p = \frac{RT}{v-b} = \frac{a}{(v+b)(v+b+2c) + (b+c)(v-b)} \quad (2)$$

The energy parameter of component  $i$  is estimated by

$$a_i = \Omega_a \frac{R^2 T_{ci}^2}{P_{ci}} a(T_{ri}) \quad (3)$$

$$a(T_{ci}) = \left[ 1 + a_o (1 - \sqrt{T_{ri}}) + a_1 + a_2 (1 - T_r)(0.7 - T_r) \right]^2 \quad (4)$$

For non-polar (hydrocarbon) components,  $\alpha_1, \alpha_2$  are equal to zero, for the PR EOS (1978),  $\alpha_0$  is giving by:

$$a_0 = (0.3764 + 1.5422\omega_i - 0.2699\omega_i^2), \quad \omega_i \leq 0.49 \quad (5)$$

$$a_0 = (0.379642 + 1.4850\omega_i - 0.164423\omega_i^2 - 0.016666\omega_i^3), \quad \omega_i \geq 0.49. \quad (6)$$

$$b_i = \Omega_b \frac{R^2 T_{ci}^2}{P_{ci}} - c_i \quad (7)$$

where  $c_i$  = the volume-shift parameter of component  $i$ , for the Peng-Robinson:  $\Omega_a = 0.457236$ ,  $\Omega_b = 0.077796$ . The dimensionless volume shift parameter  $s_i$  is defined as

$$s_i = \frac{c_i}{b_i + c_i} = \frac{c_i}{\Omega_b \frac{RT_{ci}}{P_{ci}}} \quad (8)$$

The volume shift parameters are determined by matching the

experimental density data at  $T_r=0.7$  for a lot of components, the  $s$  values are stored in the simulation. If the values are not available, the parameters for light components are calculated by Peng-Robinson EOS:

$$s_i = 0.4772 w_i - 0.154700 \quad (9)$$

For a heavy component, the volume shift parameters are determined by matching its specific gravity (SG) at standard conditions. Application of the EOS to fluid mixtures requires a mixing rule in order to describe the mixture from the properties of its pure constituents. For hydrocarbon systems, the Van-Dar-Waal's mixing rules are commonly used, here it is used with only temperature independent  $d_{ij}$

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (10)$$

$$b = \sum_i z_i b_i \quad (11)$$

$$c = \sum_i z_i c_i \quad (12)$$

The  $d_{ij}$  are usually referred as Binary Interaction Parameters (BIP) and are usually calculated by parameterizing the EOS with experimental K-values. The BIP values in the simulation and the alternative method for evaluating BIPs were proposed by Mehra (1981) and Li (1983) [23]:

$$d_{ij} = \left[ 1 - \left( \frac{\sqrt{v_{ci}^{1/2} v_{cj}^{1/2}}}{v_{ci}^{1/2} + v_{cj}^{1/2}} \right)^n \right] \quad (13)$$

where  $n=1$  (constant) and  $v_{ci}$  = The critical molar volume of the component  $i$ . The critical properties of the heaviest component together with the binary interaction parameter were used as regression variables to fit provided thermodynamic properties of the fluid and pressure saturation data. Table I shows reservoir fluid components and Table II shows predicted PVT properties. On the other hand, asphaltene precipitation is modelled using a multiphase flash calculation in which the fluid phases are described with an equation of state and the fugacities of components in the solid phase are predicted using the solid model. The approach for modeling asphaltene precipitation is described [24], [25]. The precipitated phase is represented as an ideal mixture of solid components [23]. The fugacity of a precipitating component in the solid phase is:

$$\ln f_s = \ln f_s^* + \frac{v_s}{R} \left[ \frac{p - p_{tp}}{T} - \frac{p^* - p_{tp}}{T^*} \right] - \frac{\Delta H_{tp}}{R} \left[ \frac{1}{T} - \frac{1}{T^*} \right] - \frac{\Delta C_p}{R} \left[ \ln \left( \frac{T^*}{T} \right) - T_{tp} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (14)$$

where  $f_s$  is the fugacity at pressure  $p$  and temperature  $T$ ,  $f_s^*$  is the fugacity at pressure  $p^*$  and temperature  $T^*$ ,  $\Delta H_{tp}$  is the heat of fusion at the triple point,  $\Delta C_p$  is the solid-liquid heat capacity

difference,  $p_{tp}$  and  $T_{tp}$  are the triple point pressure and temperature, and  $R$  is the universal gas constant. For isothermal predictions, this equation can be simplified to give:

$$\ln f_s = \ln f_s^* + v_s \left( \frac{p - p^*}{RT} \right) \quad (15)$$

TABLE I  
RESERVOIR FLUID COMPONENTS

Comp	Pc (psi)	Tc (F)	Mol Wt. (lb/lb-mol)	Mol. Frac (%)
N <sub>2</sub>	492.3	-232.50	28.013	0.00116
CO <sub>2</sub>	1069.9	87.90	44.010	0.00760
CH <sub>4</sub>	667.1	-116.59	16.043	0.40392
C <sub>2</sub> -C <sub>3</sub>	665.7	142.97	35.170	0.24940
C <sub>4</sub> -C <sub>6</sub>	493.7	370.50	69.030	0.12738
C <sub>7</sub> -C <sub>12</sub>	361.5	591.35	120.20	0.13768
C <sub>13</sub> -C <sub>19</sub>	245.4	836.87	222.91	0.04242
C <sub>20+</sub>	146.9	1170.6	427.33	0.03040

TABLE II  
PREDICTED PVT PROPERTIES

PVT Properties	Sample	Model	AARE (%)
Sat. Press. (psi)	2652	2652.003	0.0001
Viscosity (cp)	0.270	0.2698	0.0741
Oil Density (lb/ft <sup>3</sup> )	36.849	36.900	0.1384
AARE (%)			0.0709

The crucial step in modeling asphaltene precipitation is the characterization of the solids forming components, both in solution and in the solid phase. Furthermore, the BIP between the light components and the asphaltene component have significant impact on the prediction of the asphaltene precipitation. A greater value for BIP between light components and asphaltene will cause a superior amount of asphaltene precipitation [10]. In this study, the amount of asphaltene precipitation was 0.26 wt.% at the onset pressure of 2702 psi and 238 °F. Fig. 3 shows asphaltene precipitation curve after correcting BIP between the lighter components (C<sub>1</sub> - nC<sub>5</sub>) and asphaltene component to get the precise shape of the precipitation curve. Reservoir fluid components are shown in Table III and calculated mole fraction of the asphaltene component is shown in Table IV, whereas Fig. 4 shows phase envelope for the asphaltene. However, it was found that by splitting the heaviest component into two components, as a non-precipitating and a precipitating fraction, these two components have the same critical properties and acentric factor. Therefore, the mole fraction of heaviest component (non-precipitating) and asphaltene component (precipitating) can be calculated by:

$$\text{Mole \%}(asph) = \text{weight \%}(asph) \frac{\overline{MW}_{Oil}}{\overline{MW}_{Asph}} \quad (16)$$

$$\overline{MW}_{Oil} = \sum Y_i MW_i \quad (17)$$

Additionally, solubility of CO<sub>2</sub> and hydrocarbon components in the aqueous phase is computed by Henry's law. Reference

Henry's constant, molar volume at infinite dilution, and reference pressure are the properties used in calculating the solubility of CO<sub>2</sub> in the aqueous phase. Henry's constants are calculated from:

$$\ln H_i = \ln H_i^0 + \frac{v_i^\infty (p - p_i^0)}{RT} \quad (18)$$

where the superscript "o" refers to the reference condition. If the experimental solubility data are to be matched using regression, this method for defining the solubility parameters must be used.

However, the Oil-Gas-Water (OGW) calculation involves a three-phase calculation where the vapor and liquid phases are modeled with an EOS, while the aqueous phase is modeled with Henry's law. Li and Nghiem [26] recommended the use of Henry's law constants for component solubility in the aqueous phase. The fugacity coefficient of component *i* in the aqueous phase  $\phi_{iw}$  is given by

$$\ln H_i \phi_{iw} = \ln \left( \frac{H_i}{P} \right) \quad (19)$$

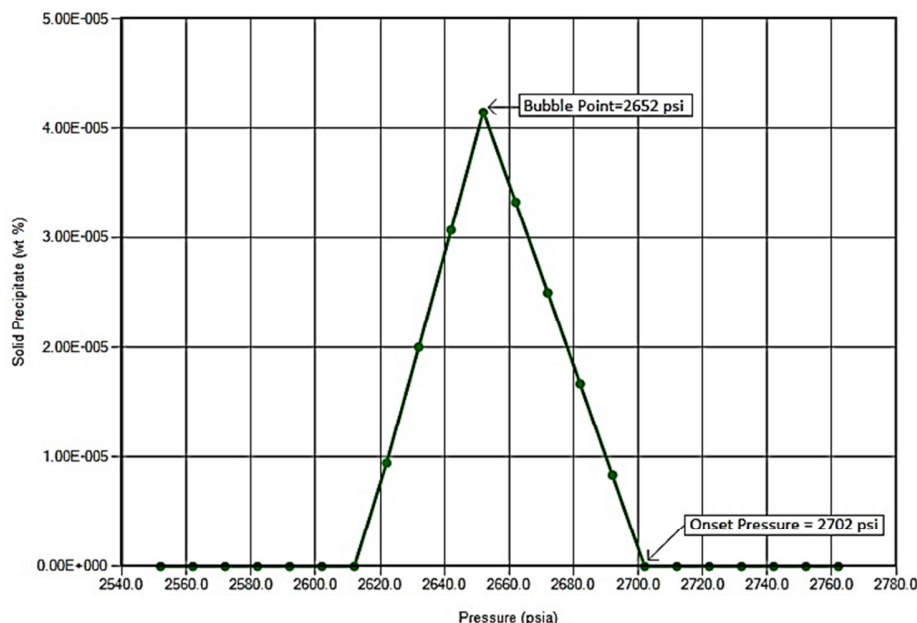


Fig. 3 Asphaltene precipitation curve

TABLE III  
RESERVOIR FLUID COMPONENTS

Comp	Mol. Fract. (%)	MWi	YiMWi
N <sub>2</sub>	0.001189987	28.010	0.03333511
CO <sub>2</sub>	0.007599917	44.010	0.33447235
CH <sub>4</sub>	0.403915588	16.040	6.48001777
C <sub>2</sub> H-nC <sub>5</sub>	0.364326024	45.140	16.4449706
C <sub>6</sub> -C <sub>12</sub>	0.150098365	120.35	18.0648125
C <sub>13</sub> -C <sub>19</sub>	0.042429536	213.30	9.05036095
C <sub>20</sub> -C <sub>25</sub>	0.012752971	310.31	3.95731101
C <sub>26</sub> -C <sub>30</sub>	0.006436305	388.60	2.50116104
C <sub>31</sub> -C <sub>35</sub>	0.004093723	458.73	1.87792182
C <sub>36</sub> -C <sub>43</sub>	0.003685617	545.83	2.01170178
C <sub>44+</sub>	0.003469911	763.62	2.64970750
Asph	0.000002069	763.62	0.00157966

Moreover, water modeling in GEM does not allow vaporization of the water component. water density is calculated from a linear model in terms of compressibility where water viscosity is constant [23]. Though, Rowe-Chou aqueous density correlation and Kestin aqueous viscosity correlation are used to allow the water density and water viscosity in GEM to be calculated respectively as a function of pressure, temperature, and salinity. CMG-WinProp usually

estimates solubilities for all components up to C<sub>8</sub>. However, in this study, it is desired to model only the solubility of CO<sub>2</sub> in the aqueous phase. Brines are modeled by assuming that the total salinity is due only to Na<sup>+</sup> and Cl<sup>-</sup> ions and the total salinity of the brine is 100,000 ppm. Therefore, Henry's constant calculated for both CO<sub>2</sub> and H<sub>2</sub>O while considering rest of the components as insoluble. Table V shows reservoir fluid components and calculated solubility properties.

TABLE IV  
MOLE FRACTION OF THE ASPHALTENE COMPONENT

Weight % of Asph.	0.26
Asph MW	763.62
Ave. MW <sub>oil</sub> (Mol. %)	99.652802
Σ YiMWi	60.7560654
C <sub>20+</sub> & Asph (Mol. %)	0.347198
C <sub>20+</sub> (Mol. %)	0.346991
Asph. (Mol. %)	0.00020686

### B. Rock Properties

A dual-permeability model was built in computational domain consisting of an ideal-fracture with a width of 1 ft and a permeability of 40-mD, instead of a real fracture with a permeability of 40,000-mD and 0.001-ft width, in order to

reduce computational time and numerical complexity [20]. The horizontal well was drilled and perforated along its complete length, and the entire production horizon was fixed for five years, bottom-hole production pressure kept constant at 2000 psi and bottom-hole injection pressure at maximum 7000 psi were used in simulation. As shown in Table VI and Fig. 5, domain main properties and relative permeability curves were used in this study, respectively. The ideal-fracture permeability,  $k_{ideal}$  is calculated by [27]:

$$k_{ideal} = \left( \frac{k_f w_f}{w_{ideal}} \right) \quad (20)$$

where  $w_f$  is the real-fracture width,  $k_f$  is the real-fracture permeability, and  $w_{ideal}$  is the ideal-fracture width used in the simulator. Fig. 6 shows the comparison between real-fracture and ideal-fracture. Thus, this procedure can reduce the simulation running cost and time

### III. RESULTS

#### A. Effects of Different Parameters on Oil Recovery

The study of cyclic CO<sub>2</sub> injection and hydrocarbon recovery in ultra-low permeability reservoirs is mainly a function of several parameters: firstly, the structural parameters such as fracture conductivity, fracture half-length, fracture spacing, and matrix porosity [28]; secondly, the operational parameters such as bottom-hole pressure, primary depletion time, CO<sub>2</sub> injection time, and number of cycles. However, the most important parameter in the oil industry is bottom-hole pressure of an oil well at any existing operating condition and its relation within the formation pressure, in order to determine the most efficient

methods of recovery and lifting procedure. Thus, it increases oil production, eliminates sand production by controlling the drawdown, adjusts injection rates, optimizes operational costs, and determines the natural drive mechanisms in the reservoir. Fig. 7 (a) shows the effects of minimum bottom-hole production pressure on the oil recovery. As the oil-well kept on producing, the reservoir pressure started declines smoothly with oil production. However, as the reservoir pressure drops below the bubble pressure 2652 psi, higher oil recovery was observed about 11.53% of original oil in place at pressure 2000 psi; this due to the solution gas which was dissolved in the oil, becomes free gas and drives the crude oil to the wellbore. However, further decline in the reservoir pressure up to 500 psi showed reduction in the oil recovery due to alleviation of gas drive mechanism. Therefore, in this work, the baseline was created at 2000 psi as minimum bottom-hole production pressure to be used for further assessment of other parameters effecting cyclic CO<sub>2</sub> injection in tight oil reservoirs.

TABLE V  
 RESERVOIR FLUID COMPONENTS FOR SOLUBILITY OF CO<sub>2</sub> IN THE BRINE

Comp	Mol. Frac (%)	Ref. Henry (atm)	Vol. info (l/mol)	Pres. ref (atm)
N <sub>2</sub>	0.0006	Insoluble	0.03320	34.02
CO <sub>2</sub>	0.0038	4296.91	0.02913	34.02
CH <sub>4</sub>	0.2020	Insoluble	0.03656	34.02
C <sub>2</sub> H-C <sub>3</sub> H	0.1247	Insoluble	0.05323	34.02
C <sub>4</sub> -C <sub>6</sub>	0.0637	Insoluble	0.07264	34.02
C <sub>7</sub> -C <sub>12</sub>	0.0688	Insoluble	0.09221	34.02
C <sub>13</sub> -C <sub>19</sub>	0.0212	Insoluble	0.09223	34.02
C <sub>20+</sub>	0.0152	Insoluble	0.86631	34.02
H <sub>2</sub> O	0.5000	1.651498	0.01898	34.02

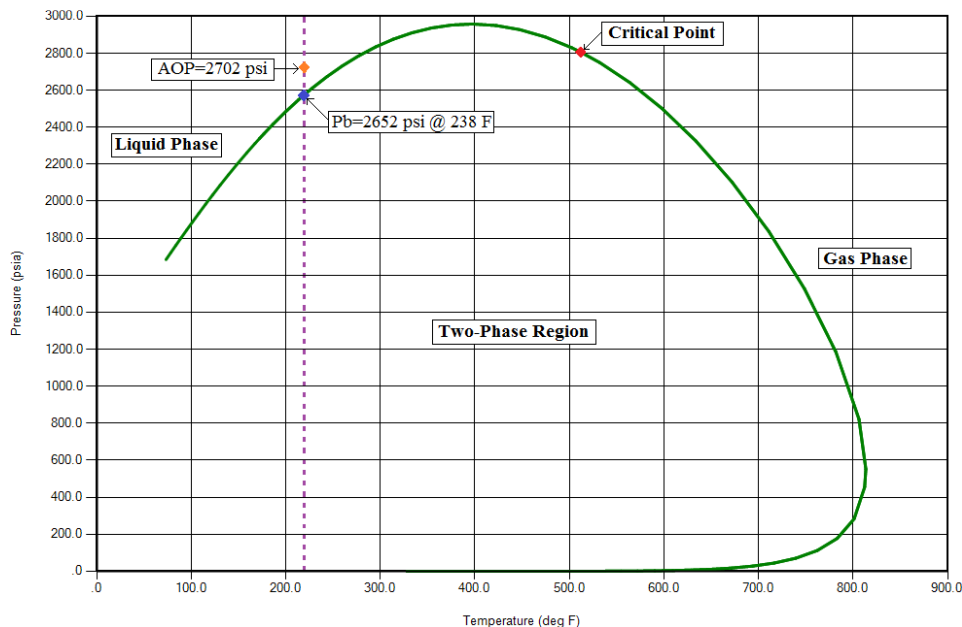


Fig. 4 Asphaltene phase envelope

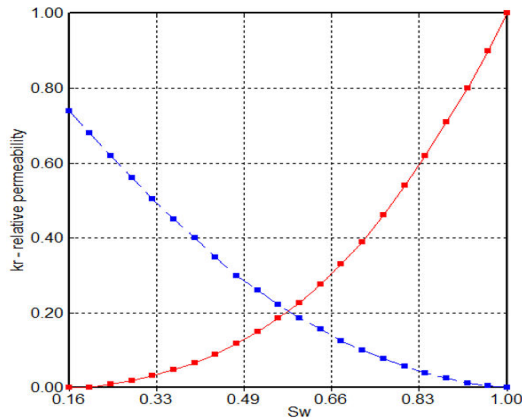


Fig. 5 Relative permeability curves

In order to evaluate the performance of cyclic CO<sub>2</sub> injection process based on the primary depletion period, the different time steps are chosen for primary production. As noted from Fig. 7 (b), the early CO<sub>2</sub> injection has less impact (positive) on oil recovery about 14.5% of OOIP, whereas delaying CO<sub>2</sub> injection has no further effect on the incremental oil recovery; therefore, the best time for CO<sub>2</sub> injection as observed is to be after 18 months with highest oil recovery around 16% of OOIP. Thus, the results perfectly matched the primary recovery of unconventional reservoirs which remains low at only 5-8% of OOIP, even though long horizontal wells have been drilled and massively fractured as reported by Department of Mineral Resources, North Dakota, USA [4]. Number of cycles is also an important parameter of the cyclic CO<sub>2</sub> injection process. As shown in Fig. 7 (c), the oil production boosted with increase in

the number of cycles. However, the oil recovery from primary production was about 11.53%, whereas the incremental oil recovery of the first two cycles was approximately 2.8%. Moreover, the incremental oil recovery from the rest of the cycles (third to sixth) produced only 3.8%. Thus, the oil recovery declined in the later cycles might be due to the reduction in CO<sub>2</sub> efficiencies or diminish of the oil in the reservoir. On the other hand, existence of fissures or induced hydraulic fractures provides a large contact area for the CO<sub>2</sub> to diffuse through and penetrate into the low-permeability formation.

TABLE VI  
 DOMAIN MAIN PROPERTIES

Properties	Value	Unit
Matrix Porosity	0.05	%
Fracture Porosity	0.001	%
Matrix Permeability	0.01	mD
Fracture Permeability	0.002	mD
Hydraulic Fracture Permeability	40000	mD
Ideal-Fracture Permeability	40	mD
Hydraulic Fracture width	0.001	ft
Ideal-Fracture width	1.00	ft
Hydraulic Fracture spacing	200	ft
Initial Reservoir Pressure	5820	psi
Minimum Production Pressure	1000	psi
Maximum Injection Pressure	7000	psi
Reservoir Temperature	238	°F
Reservoir Depth	8500	ft
Initial Water Saturation	0.16	%

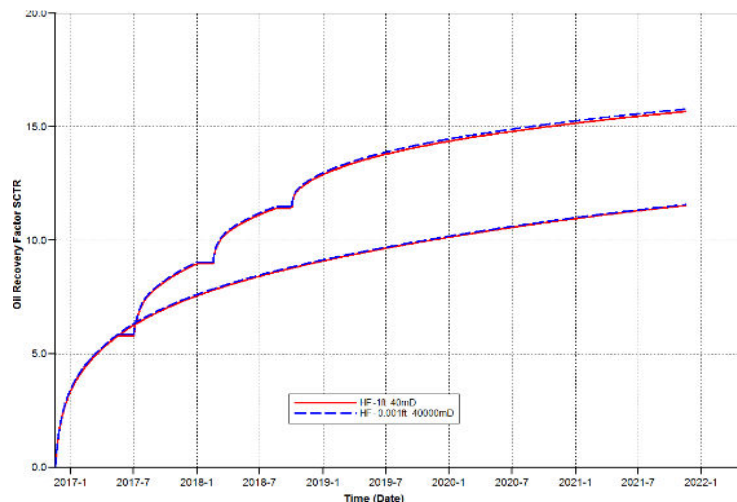


Fig. 6 Comparison between real fracture and ideal-fracture

Generally, natural fractures in the matrix are not connected to each other. Therefore, they are considered as non-productive unless they have been linked to hydraulic fractures. In order to evaluate the effect of hydraulic fracture spacing on the oil recovery, hydraulic-fracture half-length was kept constant at 200 ft, while hydraulic-fracture spacing varied in order to influence the oil recovery. As can be seen from Fig. 7 (d), the

nearer spacing between the fractures leads to a higher oil recovery than those having wider spacing during cyclic CO<sub>2</sub> injection process. Furthermore, the hydraulic fracture half-length plays an important role in recovering more oil from ultra-low permeability reservoirs. The longer fracture half-length connects with a larger portion of the reservoir volume allowing more CO<sub>2</sub> to diffuse and penetrate into the

formation matrix, resulting in higher oil production. As observed from Fig. 7 (e), this incremental oil recovery is further enhanced as the fracture half-length is increased. The unconventional recourses have complicated characteristics such as micro-fractures, natural fracture and ultra-low permeabilities were varying from micro to nano-Darcies. In such reservoir, the fluids flow from matrix to the natural

fracture, from natural fracture to the hydraulic fracture and from hydraulic fracture to the wellbore. Fig. 7 (f) shows the effects of natural fracture permeability on the oil recovery. It is noted that, if reservoir natural fracture permeability is improved from 0.002 mD to 0.2 mD, the incremental oil recovery will boost sharply due to high conductivity path for the oil to flow easily from formation to the wellbore.

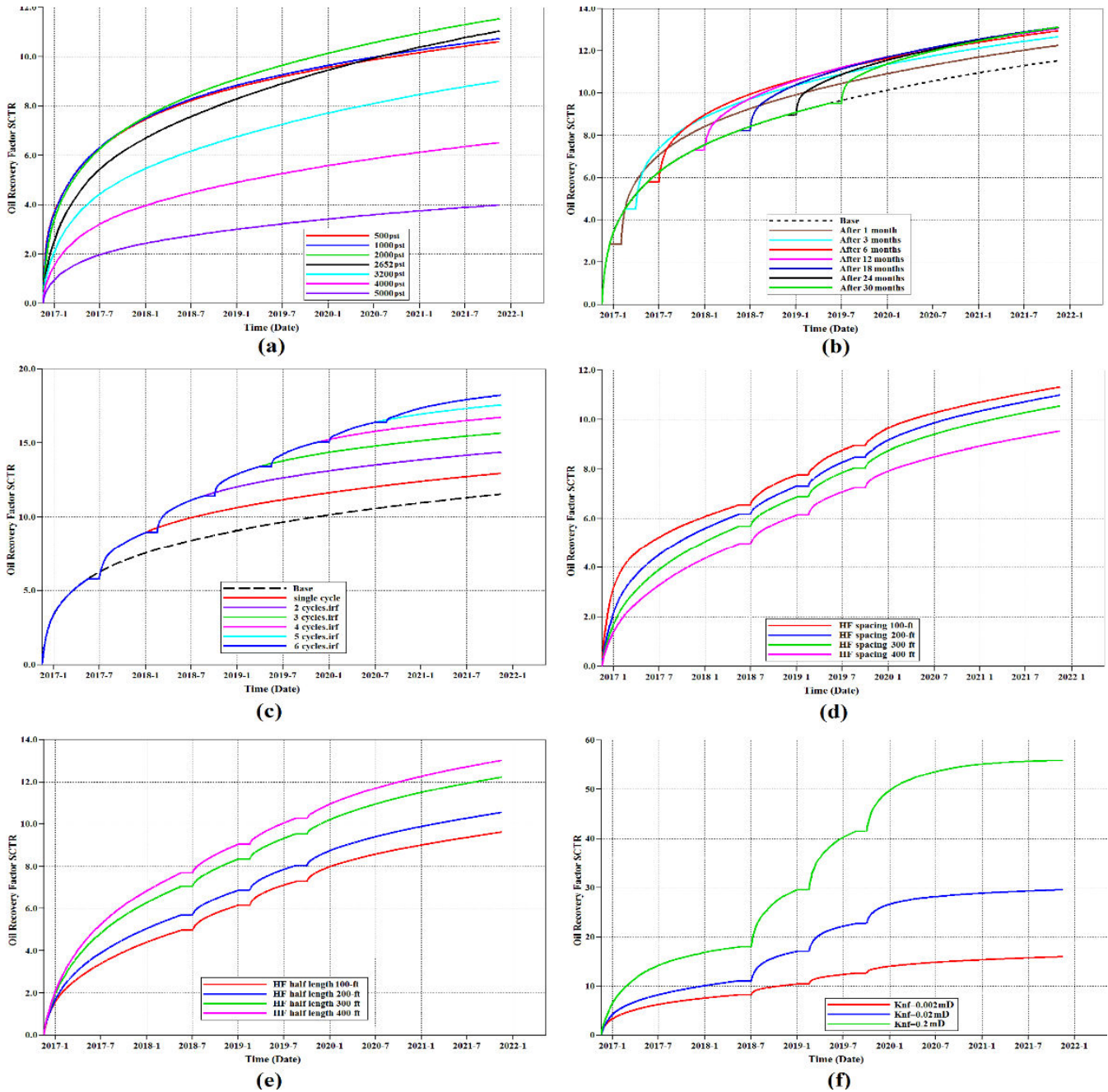


Fig. 7 Effects of different structural and operational parameters: (a) effects of BHP (b) effects of primary depletion effect (c) effects of number of cycles (d) effects of HF spacing (e) effects of HF half-length and (f) effects of NF permeability on the oil recovery

### B. Cyclic CO<sub>2</sub> Injection Process

During cyclic CO<sub>2</sub> injection process, CO<sub>2</sub> is injected into the reservoir at a certain pressure. The injection wells are shut-in to allow CO<sub>2</sub> and crude oil to soak for a period of time prior to

being switched back on for the production as shown in Fig. 8. This single cycle may be repeated for a couple of times until an economical production level is achieved. CO<sub>2</sub> behaves as a supercritical fluid under most reservoir conditions (gas-like

viscosity and liquid-like density) allowing superior volume of CO<sub>2</sub> to be stored in the reservoir, causing crude oil volume to swell, its viscosity is decreased, interfacial tension is reduced, crude oil is driven by solution oil gas, and light-components are extracted to the injected CO<sub>2</sub> phase, and thereby improves oil displacement efficiency. Moreover, the CO<sub>2</sub> diffusion mechanism during soaking period is considered as the fracture is saturated with the injected gas (CO<sub>2</sub>), and the low-permeability matrix is saturated with the reservoir fluid (oil). It is assumed that there were no viscous forces, gravity, and capillary pressure between two phases in the fracture and matrix. However, there is only difference of gradient mass or concentration of CO<sub>2</sub> and components in the oil and gas phases [29]. Fig. 9 shows CO<sub>2</sub> diffusion mechanism during soaking period. As the CO<sub>2</sub> mass fraction was greater than 0.3, significant impact on the saturation pressure has become greater due to the interaction between the hydrocarbon molecules which were affected in such a way that a heavy phase isolates the light hydrocarbon fraction in the form of vapor

phase as the pressure is lowered; the system was divided into three phase fractions as shown in Fig. 10: the light phase (gas), the intermediate phase (CO<sub>2</sub> rich-liquid), and heavy oil phase (oil rich-liquid), leading to oil swelling and viscosity reduction, as it was observed from our previous lab work [30], [31].

The determination of the above-mentioned design constraints to optimize the injection process is a difficult job. In order to evaluate the effects of the individual period (injection, shut-in or production) on the oil recovery, the other two periods were kept constant. Table VII shows three different cases for each period, and the analysis is summarized in Fig. 11 where the oil recovery factor boosted from 18% as planned study (red line) to 22.5% as optimized study (green line) with overall 4.5% increment in oil recovery. One can conclude that more CO<sub>2</sub> injection will lead to more oil recovery, and the production period mostly depends on the injection period, whereas the soaking period has specific period and further extending the soaking period would not affect any additional increment on the oil recovery.

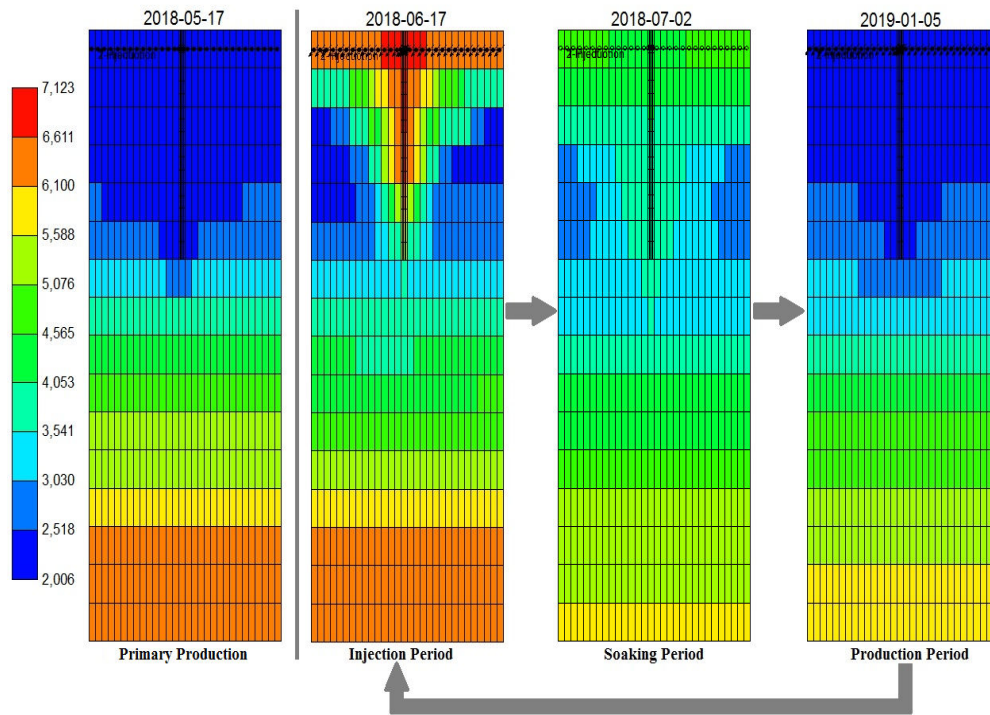


Fig. 8 Cyclic CO<sub>2</sub> injection process

### C. Sensitivity Study of Cyclic CO<sub>2</sub> Injection Process

The uncertainty in tight reservoir is due to the several parameters including reservoir permeability, number of hydraulic fractures, fracture half-length, and fracture conductivity. Additionally, the parameters associated to cyclic CO<sub>2</sub> injection process are also uncertain, including CO<sub>2</sub> injection period, soaking period, number of cycles, and CO<sub>2</sub> diffusivity. Hence, seven uncertain parameters were investigated. It is concluded that the oil recovery factor increases with increase in the CO<sub>2</sub> injection period, followed by number of cycle, CO<sub>2</sub> diffusion, CO<sub>2</sub> soaking time,

permeability, and fracture half-length, while it decreases with increasing fracture conductivity [32]. The effects of uncertain parameters on oil recovery factor are shown in Tornado plot in Fig. 12. It can be observed that the most essential parameter is CO<sub>2</sub> injection time, followed by number of cycle and CO<sub>2</sub> diffusivity.

TABLE VII  
 HUFF AND PUFF PERIODS

Huff (days)	Soaking (days)	Puff (days)
30	15	90
90	30	180
180	60	360

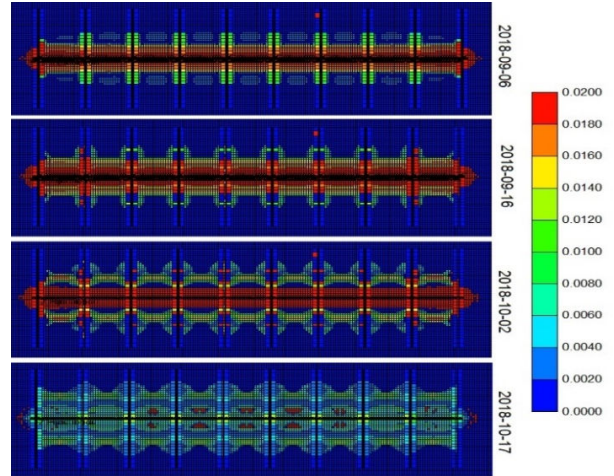


Fig. 9 CO<sub>2</sub> diffusion during soaking (shut-in) period

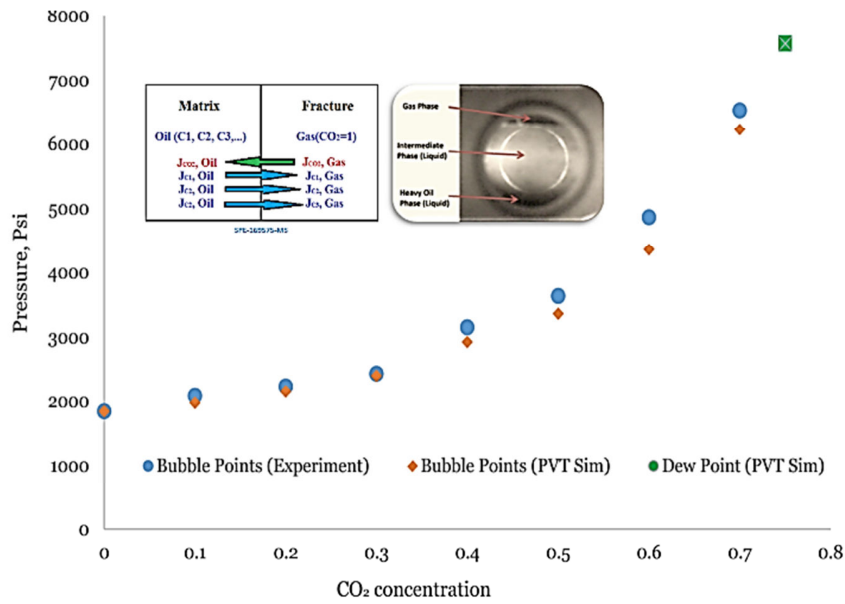


Fig. 10 Three phase system during miscibility process [30], [31]

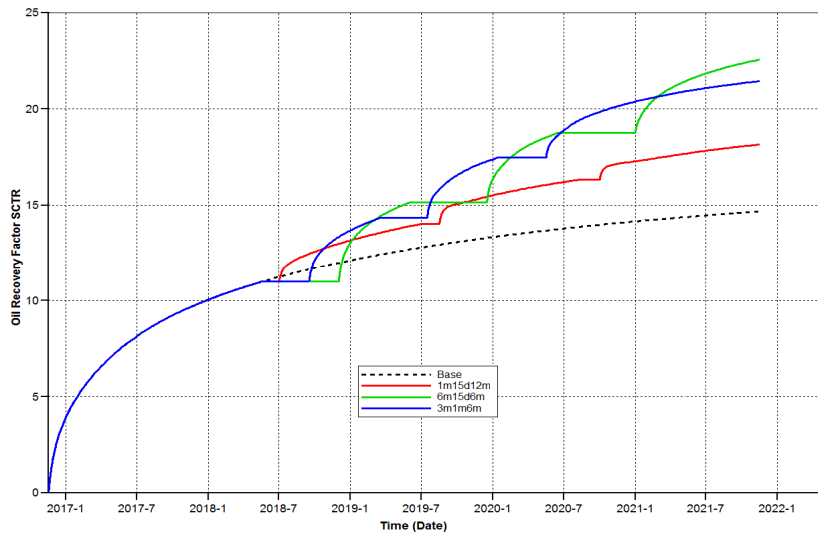


Fig. 11 Optimized cyclic CO<sub>2</sub> injection process

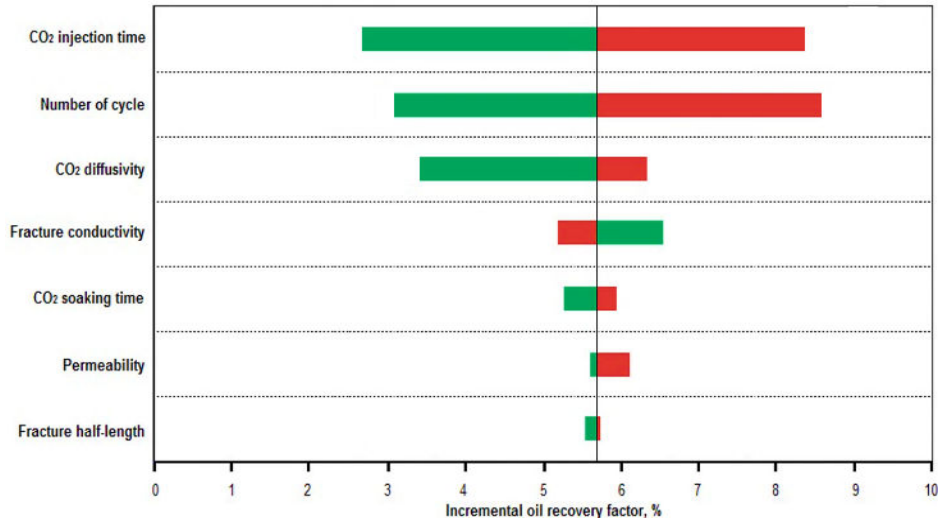


Fig. 12 Effect of uncertain parameters on oil recovery

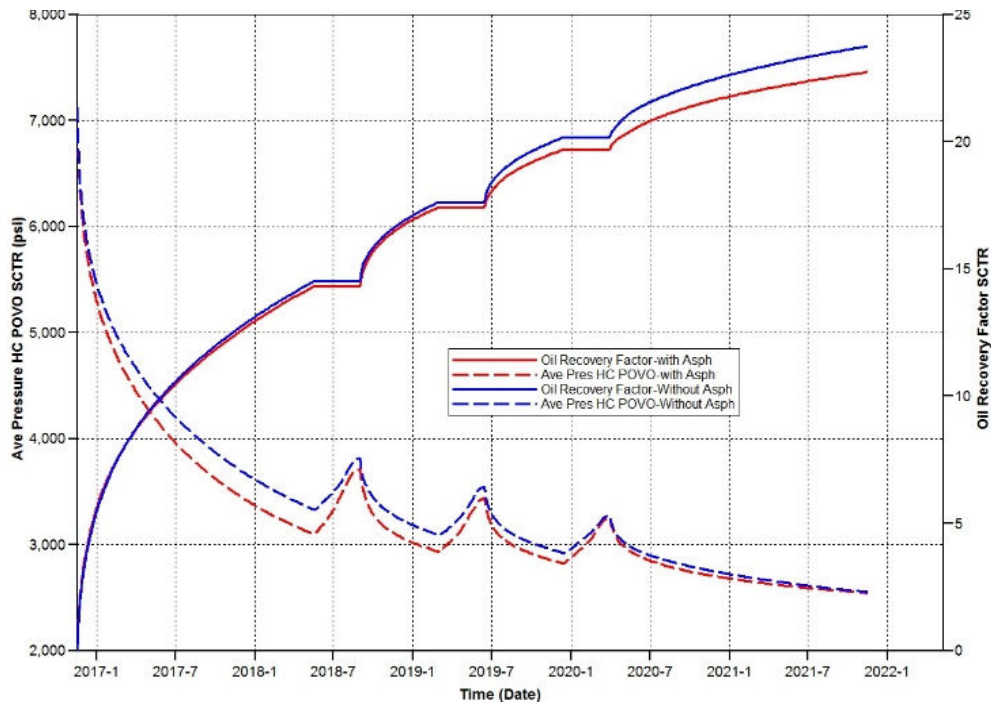


Fig. 13 Oil recovery factor and pressure drop with and without asphaltene precipitation

#### D. Asphaltene Deposition

Generally, the presence of asphaltene contents in the reservoir fluid is not an issue, but their precipitation and deposition might occur due to the miscibility process taking place between CO<sub>2</sub> with the reservoir fluid, causing an irreversible damage specially in tight oil reservoir rocks with smaller pore throats subjected to more severe formation flow impairment. In compositional modeling, it is important to select appropriate binary coefficient parameters for the sake of better prediction of asphaltene precipitation curve, and the volume shift is used to minimize the errors related to estimation of solid molar volume. However, when the bottom-hole pressure drops below the asphaltene precipitation pressure, where the average

reservoir pressure will be allowed to decrease below the bubble pressure, allowing more gas to be liberated, which in turn, reduces the solubility of asphaltene and induces precipitation. In order to prevent asphaltene precipitation, the reservoir bottom-hole pressure must be greater than asphaltene AOP 2702 psi.

The effects of the injected fluid (CO<sub>2</sub>) concentration play a significant role in preventing asphaltene deposition, the higher CO<sub>2</sub> concentration leads to higher precipitation. However, the presence of brine could also prevent asphaltene deposition, enhance the oil recovery, and reduce CO<sub>2</sub> emission. Fig. 13 shows the oil recovery factor and pressure drop with and without asphaltene, whereas Fig. 14 shows the daily oil production with and without asphaltene. As observed from

Figs. 13 and 14, the oil production rate obtained with asphaltene precipitation is lower than that of without the asphaltene precipitation. This is due to the consequences of asphaltene precipitation on permeability reduction which is mainly depending on some factors such as reservoir permeability, pore size distribution, and the amount of asphaltene deposition. In most of the situations, precipitation occurs close to the production vicinity, probably because of the pressure drop associated with the production vicinity. However, these factors may lead towards not only near wellbore formation damage, but also it might cause some formation flow impairment deep in the reservoir.

#### E. CO<sub>2</sub> Solubility in the Brine

CO<sub>2</sub> injections are used in oil industry for several options, injecting CO<sub>2</sub> into deep saline aquifers for sequestering CO<sub>2</sub> in geological formations, while injecting CO<sub>2</sub> into mature or depleted oil and gas reservoirs for the purpose of effective sequestration and enhancing production. Generally, deep saline aquifers have no economic value. In order to reduce CO<sub>2</sub> emission in the atmosphere, CO<sub>2</sub> dissolution needs to be measured under reservoir conditions. However, the solubility of CO<sub>2</sub> in the aqueous phase is mainly function of temperature, pressure, and salinity.

The volume of CO<sub>2</sub> that can be dissolved in aqueous phase can be estimated by phase behavior module (WinProp). A series of solubility curves were generated for CO<sub>2</sub> dissolutions at different pressure and temperature as shown in Fig. 15. Concerning the pressure, it can be noted that increase in pressure increases the dissolution of CO<sub>2</sub> in the aqueous phase.

However, the pressure dependency of the solubility increases as the pressure decreases. The effect of temperature on the solubility is contrary; a reduction in the temperature substantially increases the solubility, regardless of the salinity of the brine. However, at higher temperature above 251 °F, the temperature curve trend changed after 3500 psi, and CO<sub>2</sub> dissolution increased with increasing temperature. This is because the reservoir initially contains three-phase system (aqueous, liquid and vapor), and as the pressure and temperature increased, the liquid phase started evaporating and phase behavior of the fluids changed into two-phase system (aqueous and vapor) above 3500 psi, therefore the CO<sub>2</sub> dissolution increases with increasing temperature as shown in Fig. 15. Furthermore, the brine salinity (NaCl) concentration also has an impact on the CO<sub>2</sub> dissolution. Fig. 16 shows CO<sub>2</sub> solubility curves at different brine salinity (NaCl) concentrations. It can be concluded that the salinity also has a contrasting impact on the solubility as increase in the brine salinity leads to a reduction in CO<sub>2</sub> solubility, regardless of its pressure and temperature. Fig. 17 shows that the salinity of the aqueous phase is independent of pressure and temperature, using percent solubility as a function of salinity. Finally, the result obtained from CMG-GEM shows that CO<sub>2</sub> can be utilized as EOR technique as well as stored in deep aquifer CO<sub>2</sub> storage and sequestration processes. From Fig. 18, after injecting CO<sub>2</sub> in the aqueous phase, gas recovery factor (CO<sub>2</sub>) revealed negative behavior, reflecting dissolution of CO<sub>2</sub> in deep brine aquifer while enhancing the oil recovery up to some extent.

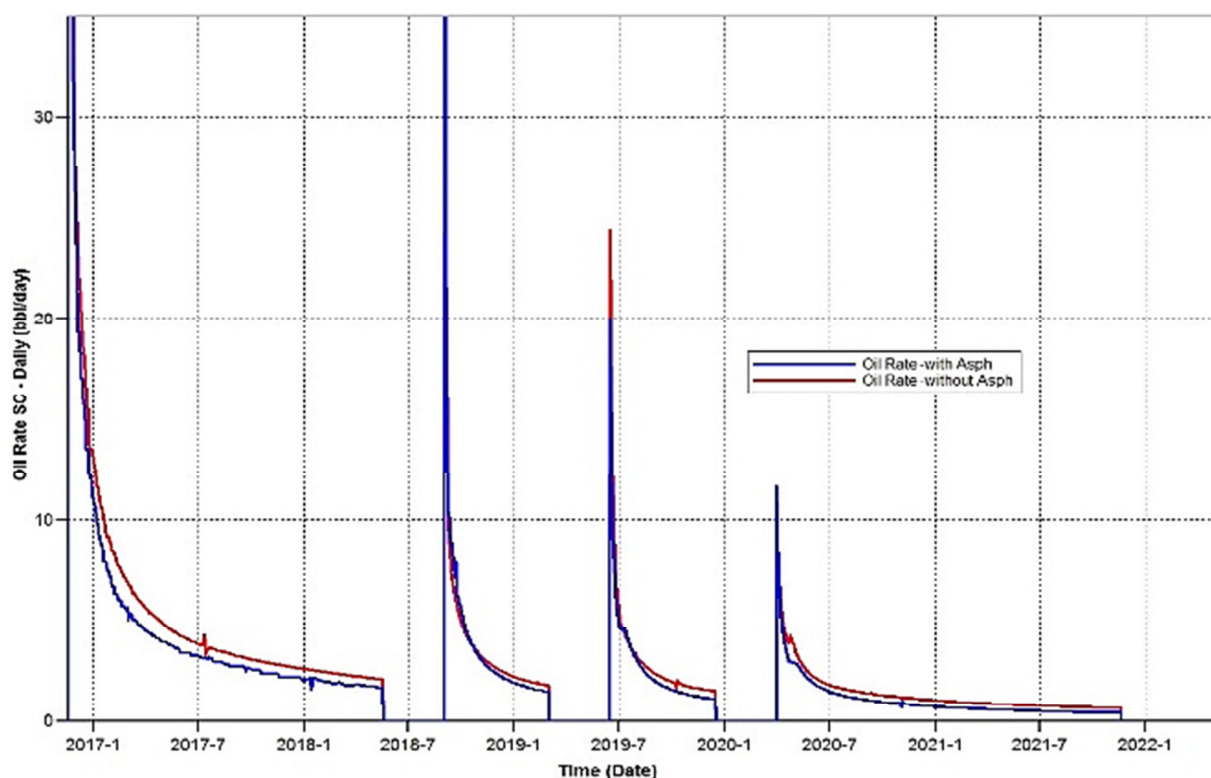


Fig. 14 Daily oil production with and without asphaltene precipitation

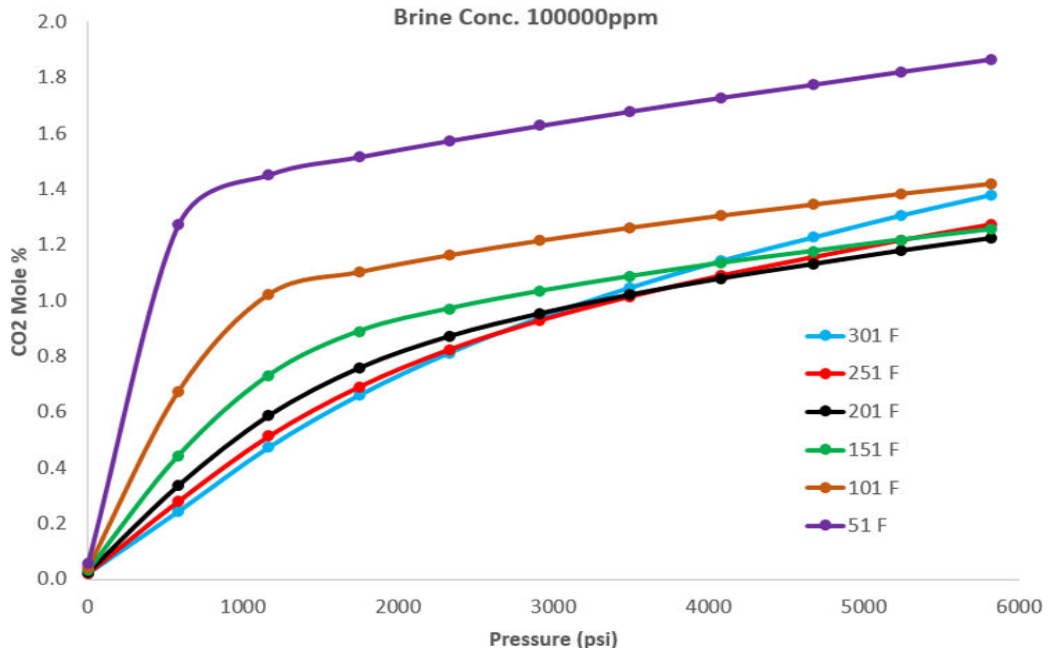


Fig. 15 CO<sub>2</sub> solubility curves at different pressure and temperature

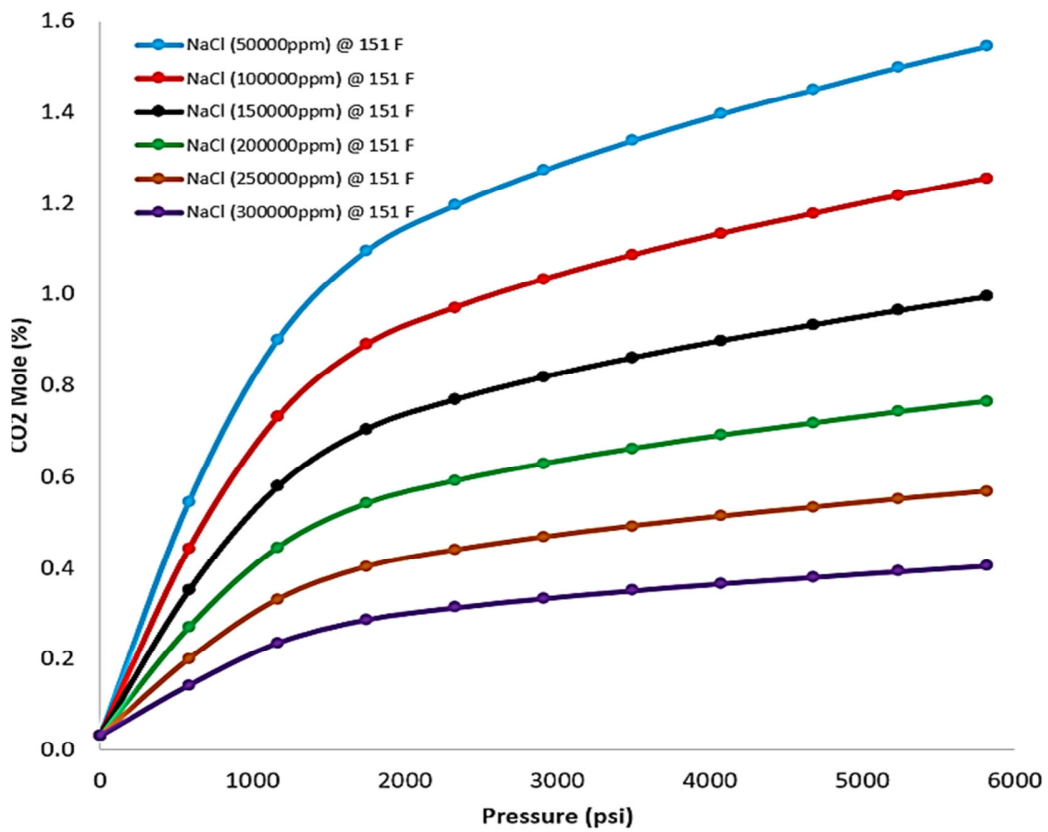


Fig. 16 CO<sub>2</sub> solubility curves at different brine salinity (NaCl) concentration

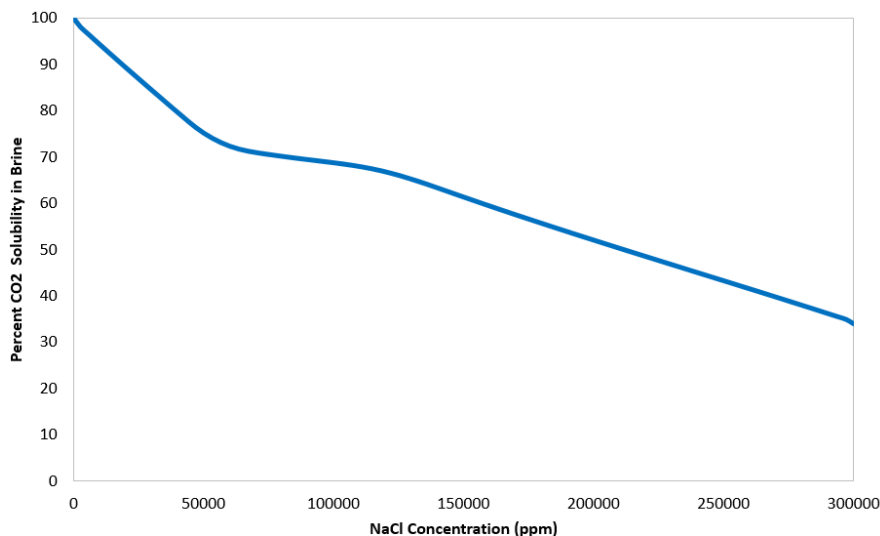


Fig. 17 CO<sub>2</sub> solubility in brine

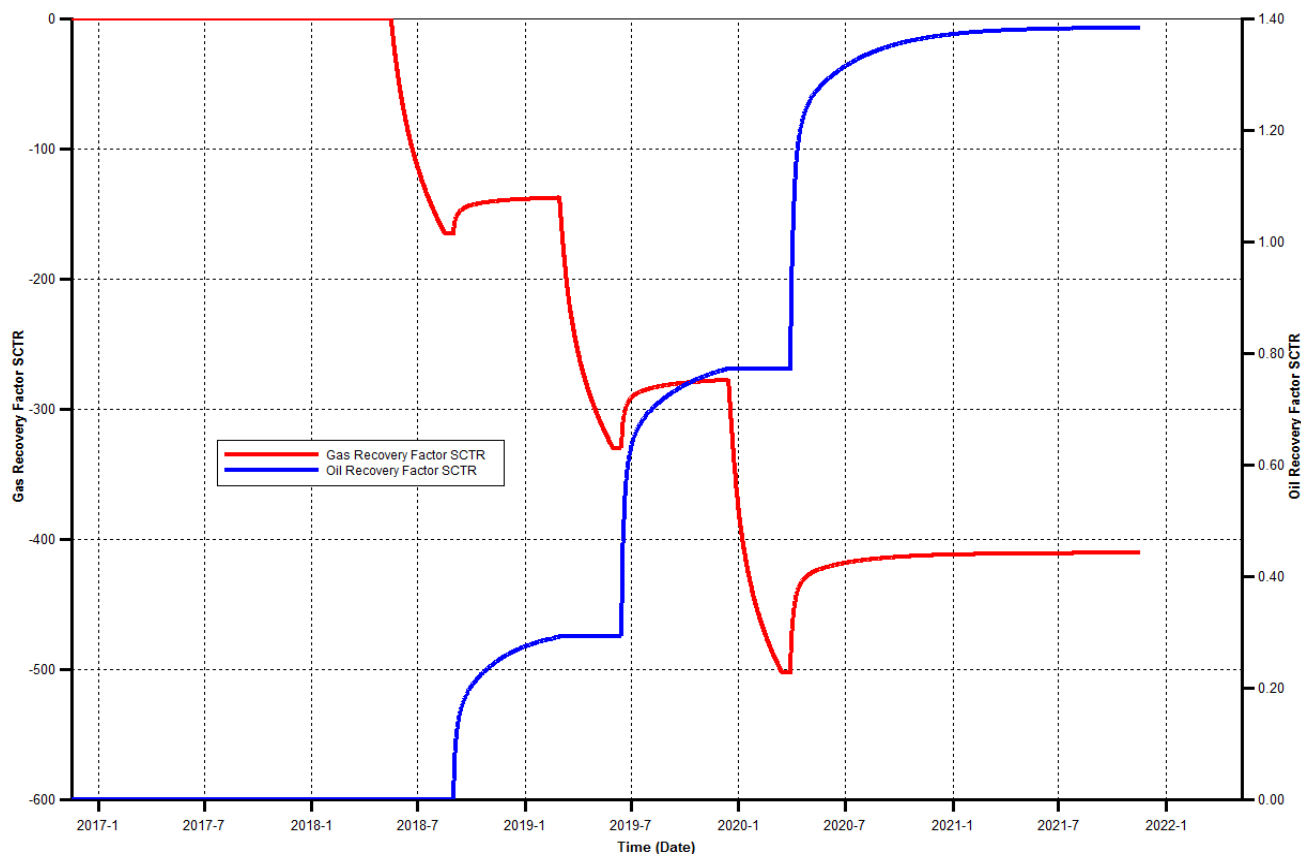


Fig. 18 Oil recovery factor and CO<sub>2</sub> recovery factor during CO<sub>2</sub> solubility process

#### IV. CONCLUSIONS

The reservoir simulation results show that cyclic CO<sub>2</sub> injection process is an effective EOR method and has ability to produce an economical amount of oil from unconventional tight reservoirs. This study acknowledged perfect procedures of optimizing the performance of cyclic CO<sub>2</sub> injection treatments and maximizing the oil recovery factor. The following conclusions can be drawn from this work:

1. Primary depletion period plays an essential role in improving oil recovery. Therefore, starting CO<sub>2</sub> injection too early or too late would adversely impact the efficiency of the process and diminish the projects net present value. So, suitable time for CO<sub>2</sub> injection in this work was observed to be after 18 months of primary depletion with highest oil recovery of about 15.94% of OOIP.
2. Higher oil recovery is expected from longer injection time

in cyclic CO<sub>2</sub> injection process, even though the production period depends on injection period, while the soaking period has specific time, and further extending soaking period would not affect an increment in oil recovery.

3. CO<sub>2</sub> diffusion during soaking period also plays an important role in penetrating the unconventional tight oil reservoirs, as it is miscible with oil, thus produces more light oil in the early life of the well.
4. Optimization of cyclic CO<sub>2</sub> injection process boosted oil recovery from 18.15% to 22.56% with overall 4.41% incremental in oil recovery.
5. The asphaltene precipitation increases as the injected fluid concentration increases.
6. Overall, CO<sub>2</sub> injection causes more asphaltene precipitated, and permeability reduction.
7. During cyclic CO<sub>2</sub> injection process, as CO<sub>2</sub> is soluble in the brine, CO<sub>2</sub> concentration is reduced and asphaltene precipitation is minimized.
8. High brine salinity leads to a reduction of CO<sub>2</sub> solubility.
9. The dissolution of CO<sub>2</sub> in the brine aquifer increases with increasing pressure and decreasing temperature.
10. The CO<sub>2</sub> solubility in the aquifer increases with decreasing brine salinity.

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