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Compositional Modeling to Analyze the Effect of CH₄ on Coupled Carbon Storage and Enhanced Oil Recovery Process

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Abstract: The present study is aimed at the development of compositional simulation models of the co-injection of CO₂ and CH₄ during the water-alternating-gas (WAG) process in order to assess the efficiency of carbon capture and storage in combination with enhanced oil recovery (CCS-EOR). The co-injection of CO₂ and CH₄ occupies more reservoir pore volume and causes higher reservoir pressure than CO₂ WAG, thus leading to an enhanced early EOR performance. However, the overall EOR performance of the co-injection method becomes lower than that of CO₂ WAG due to the reduced miscibility and sweep efficiency upon further CH₄ addition. The decrease in gas displacement and sweep efficiency weaken the hysteresis effects upon the residual trapping mechanism. However, the solubility trapping mechanism takes effect because the co-injection generates higher average reservoir pressure than does the CO₂ WAG. The index of global warming potential (GWP) in a mole unit is employed to quantify the carbon storage effects of CO₂ and co-injection WAG cases. According to the index, 1 mole of CH₄ sequestration has the same effects as that of 10 moles of CO₂ for global warming mitigation. In conclusion, the carbon storage effects are enhanced as CH₄ concentration in the WAG increases.

Keywords: carbon capture and storage associated with enhanced oil recovery (CCS-EOR); CH₄; water alternating gas (WAG); global warming potential (GWP)

1. Introduction

Carbon capture and storage (CCS) has become well-known as a technology for reducing the emission of greenhouse gases from fossil fuels during power generation and industrial processes [1]. Projects involving the injection of carbon dioxide (CO₂) for enhanced oil recovery (EOR) have been operating worldwide since the early 1970s [2] and EOR is expected to be a major driver for CCS by providing an additional revenue stream. Hence, combining the CO₂-EOR and CCS into a coupled CCS-EOR approach provides a synergistic effect towards business and environmental protection by offering commercial opportunities to oilfield operators. Consequently, almost 80 million tons (Mt) of CO₂ are already being used for CCS-EOR each year [3,4].

Methane (CH₄) is generated as a by-product of oil extraction during primary and secondary oil production and EOR. As CH₄ is a potent greenhouse gas (GHG), the operator often chooses to flare this by-product instead of releasing it directly to the atmosphere if there is little commercial opportunity or

sufficient regulatory incentive to bring it to market [5]. Also, CH₄ has been used as a re-injection gas for EOR [6,7]. Previous studies have examined the impacts of impurities in the CO₂ stream upon the minimum miscibility pressure (MMP) to find that the presence of CH₄ increases the MMP compared to that of CO₂, thus negatively impacting upon EOR performance [8–14]. Moreover, since the global warming potential (GWP) of CH₄ over 100 years is 28 times that of CO₂ [15], it is worth considering the use of CH₄ for CCS projects aimed at mitigating global warming and climate change. Although some studies on the geological storage of CO₂ and CH₄ in an aquifer have been conducted, there are insufficient studies examining the impact of CH₄ on CCS-EOR [16–19]. Hence, it is necessary to store CH₄ in reservoirs in order to mitigate gas flaring and release into the atmosphere by using a CCS-EOR approach that can consider energy security and climate change simultaneously. However, CH₄ affects the miscibility as well as the hysteresis and solubility effects for residual and solubility trapping mechanisms and the ultimate EOR performance during CCS-EOR.

For this reason, compositional simulation models are developed in the present study in order to investigate the effects of CO₂-CH₄ co-injection upon the CCS-EOR mechanisms and performance. The multiple-mixing-cell method is applied to calculate the MMP of the injected gases (i.e., a mixture of CO₂ and CH₄) and the reservoir oil. Of the four main CO₂ trapping mechanisms (namely: structural, residual, solubility, and mineral trapping), structural and mineral trapping are excluded from the scope of the present study due to their negligible effects upon CCS-EOR in a relatively short period [20]. Here, CO₂ can be stored in the reservoir by hysteresis and dissolution in water during the water-alternating-gas (WAG) process, thus indicating residual and solubility trapping mechanisms. A three-phase hysteresis model and Henry's law are applied for the residual trapping and solubility trapping, respectively.

2. Methodology

2.1. Calculation of Minimum Miscibility Pressure (MMP)

Carbon dioxide (CO₂) is the most common type of gas used in gas injection and has been widely used in the EOR method for light oils. Injected CO₂ acts as a solvent to reduce oil viscosity and expand oil volume in reservoirs. These phenomena occur more frequently under miscible conditions than they do under immiscible conditions [21]. As shown schematically in Figure 1, miscibility conditions during CO₂-EOR can be achieved via multiple contact processes that make use of condensing and vaporizing gas drives. At the injected CO₂ front, intermediate molecular weight hydrocarbons evaporate from the reservoir oil into the CO₂, where they equilibrate with the CO₂ to take part in the next contact with the reservoir oil in a phenomenon called the vaporizing gas drive or the forward multiple contact process. After each contact, however, the equilibrated reservoir oil behind the injected CO₂ close to the injector is continuously mixed with fresh CO₂ in a process called the condensing gas drive or the backward multiple contact process [22,23]. Due to the mass transfer of intermediate hydrocarbons between CO₂ and oil, the composition and properties, such as the density and viscosity, of the reservoir oil and injected gases are changed. This, in turn, leads to a difference in the interfacial tension (IFT) between the equilibrated oil and gas at each location. As the reservoir approaches the miscible condition, the oil viscosity and IFT decrease, such that the IFT tends towards zero and the miscible condition is reached with a reservoir pressure higher than the MMP [24].

A variety of methods, such as the slim-tube, vanishing interfacial tension, and rising bubble technique, have been conventionally employed to estimate the MMP [25–27]. However, since these methods are time-consuming, expensive, and occasionally less accurate, it is often beneficial to implement computational methods for calculating the MMP. For this purpose, the multiple-mixing-cell method using the cubic equation of state (EOS) is one of the most prevalent methods [28]. In the present study, this method is applied according to the following steps:

1. The system temperature is defined and the starting pressure for the process is estimated.
2. A calculation is performed for the displacing gas and the displaced oil to obtain the new equilibrium compositions of liquid and vapor after the first contact.

3. Step 2 is repeated for each contact using the previous and new equilibrium compositions, injected gas, and reservoir oil to obtain the updated compositions until the lengths of all key tie-lines converge to a tolerance of 10^{-8} .
4. The tie-line length is computed for the pressure and the minimum tie-line length (TL) is saved.
5. The pressure is increased and Steps 2–4 are repeated.
6. A multiple-parameter TL regression is performed to determine the exponent n , the slope m , and the constant b in the equation $TL^n = mp + b$ (power-law extrapolation), and the resulting function is plotted.
7. The MMP is determined when the power-law extrapolation gives zero to within the desired accuracy of 20 psia at the latest three pressures.

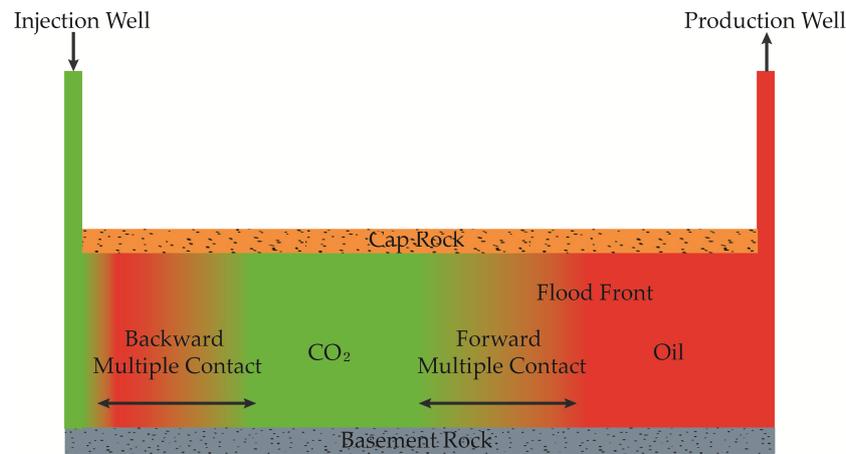


Figure 1. Schematic diagram of the multiple contact miscibility process during CO₂-enhanced oil recovery (EOR).

2.2. The Three-Phase Hysteresis Model for Residual Trapping

Although conventional two-phase hysteresis models assume the reversibility of permeability during the drainage process following the previous imbibition cycle, this assumption is invalid for three-phase fluid flow because the relative permeability of gas is lower when displacing a water-oil mixture than when displacing oil only [29]. The three-phase hysteresis model proposed by Larsen and Skauge [30] is adopted in the present study and has shown better matching to experimental data than the two-phase model [31,32].

The gas permeability during the drainage process is calculated using Equation (1):

$$k_{rg}^{drain}(S_g, S_w^I, S_g^{start}) = [k_{rg}^{input}(S_g) - k_{rg}^{input}(S_g^{start})] \left(\frac{S_{wi}}{S_w^I} \right)^\alpha + k_{rg}^{imb}(S_g^{start}) \quad (1)$$

We clarify that a list of symbols is given in the Nomenclature.

The relative permeability of the gas with decreasing gas saturation (i.e., non-wetting phase in the imbibition process) is denoted by S_{gf} and is estimated by Equations (2) and (3):

$$k_{rg}^{imb}(S_g) = k_{rg}^{drain}(S_{gf} + S_g^{end}) \quad (2)$$

$$S_{gf} = \frac{1}{2} \left\{ (S_g - S_{gr}) + \sqrt{(S_g - S_{gr})^2 + \frac{4}{C}(S_g - S_{gr})} \right\} \quad (3)$$

where the trapped gas saturation, S_{gr} , and Land’s parameter [33], C , are estimated from Equations (4) and (5), respectively:

$$S_{gr} = S_{gc} + \frac{S_{gm} - S_{gc}}{1 + C(S_{gm} - S_{gc})} \tag{4}$$

$$C = \frac{1}{S_{gr,max} - S_{gc}} - \frac{1}{S_{g,max} - S_{gc}} \tag{5}$$

$S_{gr,max}$ is the maximum trapped gas saturation and can be approximated using an empirical correlation with the porosity, ϕ [34], in accordance with Equation (6):

$$S_{gr,max} = 0.5473 - 0.9696\phi \tag{6}$$

To determine the relative permeability of the oil, the Stone’s first model modified by Aziz and Settari [35] is applied. The minimum residual oil saturation, designated S_{om} , is modified to reflect the effect of trapped gas on oil relative permeability, as shown in Equation (7):

$$S_{om}^{mod} = S_{om} - a(S_g - S_{gf}) \tag{7}$$

where S_g and S_{gf} are the total and free gas saturations respectively, and a is input parameter of 0.68 for mimicking a strongly water-wet condition [36].

2.3. Solubility Model

Carbon dioxide (CO₂) is also trapped by the solubility trapping mechanism due to contact with water. The mole fraction of CO₂ in each phase is determined from the thermodynamic equilibrium condition according to Equation (8):

$$f_{i,o} = f_{i,g} = f_{i,w} \text{ with } i = 1, \dots, n_c \tag{8}$$

where $f_{i,o}$, $f_{i,g}$, and $f_{i,w}$ denote the fugacity of the i -th component in the oil, gas, and water phase, respectively.

$f_{i,o}$ and $f_{i,g}$ are calculated using Peng-Robinson EOS [37,38]. By contrast, $f_{i,w}$ is given by Henry’s law [39] in accordance with Equation (9):

$$f_{i,w} = y_{i,w}H_i \text{ with } i = 1, \dots, n_c \tag{9}$$

where H_i and $y_{i,w}$ are Henry’s constant and the mole fraction of the i -th component in the water phase, respectively. Henry’s constant is calculated using Equations (10) and (11) under isothermal conditions [40,41]:

$$\ln H_i = \ln H_i^S + \frac{1}{RT} \int_{p_{H_2O}^s}^p \bar{v}_i dp \tag{10}$$

where R is the gas constant and T is the temperature in Kelvin. Then,

$$\ln H_i^S = \ln p_{H_2O}^s - D(T_{r,H_2O})^{-1} + E(1 - T_{r,H_2O})^{0.355} (T_{r,H_2O})^{-1} + F \exp(1 - T_{r,H_2O}) (T_{r,H_2O})^{-0.41} \tag{11}$$

where D , E , and F are constants with values of -9.4234 , 4.0087 , and 10.3199 , respectively, for CO₂, and \bar{v}_i is the partial molar volume of the i -th component at infinite dilution (cm³·mol⁻¹), which is computed using Equation (12) [42]:

$$\bar{v}_{CO_2} = -47.75418 + 4.336154 \times 10^{-1}T - 5.945771 \times 10^{-4}T^2 \tag{12}$$

where T is the reservoir temperature in K.

3. Results

3.1. Fluid Modeling

Weyburn W3 fluid data [43,44] is used as the experimental data for fluid modeling in the present study. Since the Weyburn Field in Saskatchewan, Canada, reached the economic limit of waterflooding and became a target for CO₂-EOR, extensive experiments have been conducted to investigate the interactions between oil and CO₂ for CO₂-EOR and CCS purposes [43,45].

The fluid composition of W3 experimental data and corresponding input EOS parameters used for fluid modeling are summarized in Table 1, while Table 2 presents the oil properties calculated via a regression method using the Peng-Robinson Equation of State (PR-EOS) and matched against the experimental data to increase the reliability of the compositional reservoir simulation [37,38]. The MMP is then estimated using the multiple-mixing-cell method [28]. An examination of the bottom row of Table 2 indicates that the MMP datum associated with CO₂ in W3 fluid at a reservoir temperature of 63 °C is 14,196 kPa (second column, Table 2), while the calculated value is 13,872 kPa (third column, Table 2), thus indicating a 2.3% error against the W3 data.

Table 1. Fluid composition of W3 experimental data and properties of each component used for the EOS calculation.

Component	Composition	Critical Pressure p_c (kPa)	Critical Temperature T_c (K)	Acentric Factor	Molecular Weight
N ₂	0.0207	3394.4	126.2	0.040	28.0
CO ₂	0.0074	7376.5	304.2	0.225	44.0
H ₂ S	0.0012	8936.9	373.2	0.100	34.1
Methane, C ₁	0.0749	4600.2	190.6	0.008	16.0
Ethane, C ₂	0.0422	4883.9	305.4	0.098	30.1
Propane, C ₃	0.0785	4245.5	369.8	0.152	44.1
Butane, C ₄	0.0655	3722.7	416.5	0.185	58.1
Pentane, C ₅	0.0459	3379.4	464.9	0.239	72.1
C ₆₋₉	0.2156	3019.6	556.3	0.331	102.5
C ₁₀₋₁₇	0.2202	2017.5	692.2	0.584	184.0
C ₁₈₋₂₇	0.1027	1327.0	808.4	0.893	306.2
C ₂₈₊	0.1252	1155.1	915.5	1.100	565.6

Table 2. Comparison of the W3 experimental data and fluid model properties.

Parameters	W3	Fluid Model	Difference (%)
Saturation pressure (kPa)	4920	4780	2.85
Oil density at saturation pressure (kg/m ³)	806.4	806.8	-0.05
Viscosity at saturation pressure (mPa·s)	1.76	1.75	0.57
Formation volume factor (m ³ /m ³)	1.12	1.11	0.89
API (°)	31	34.8	-12.26
MMP with CO ₂ (kPa)	14,196	13,872	2.28

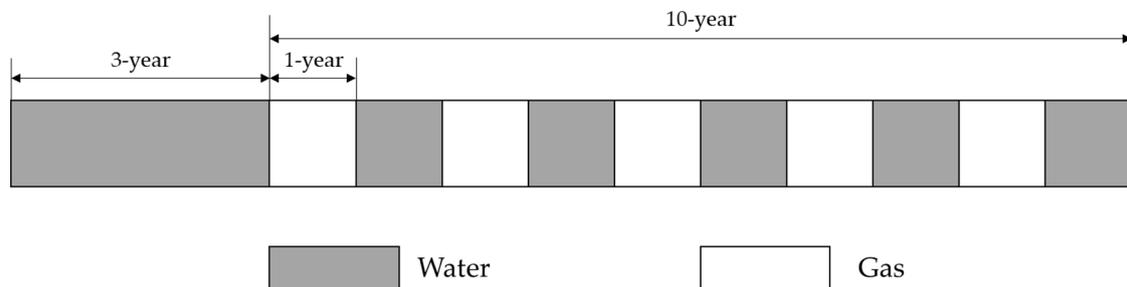
The MMPs calculated using the multiple-mixing-cell method with varying mole fraction ratios of CO₂ to CH₄ are presented in Table 3. Here, it can be seen that the MMP increases with increasing mole fraction of CH₄ in the CO₂ injection stream, thus indicating that CH₄ reduces the displacement efficiency compared to that of pure CO₂ injection, in agreement with previous experimental studies [13,14].

Table 3. Minimum miscibility pressures (MMPs) calculated using the multiple mixing cell method with various mole fraction ratios of CO₂ to CH₄.

Components	MMP (kPa)
CO ₂ 100%	13,872
CO ₂ 90% + CH ₄ 10%	21,346
CO ₂ 80% + CH ₄ 20%	22,015
CO ₂ 70% + CH ₄ 30%	22,622

3.2. Effects of CH₄ Injection on EOR Efficiency

A two-dimensional (2D) homogeneous model based on the work of Cho et al. [19] is designed to focus on investigating the miscibility and sweep efficiency without gravity override during WAG simulations. This reservoir model is discretized into $33 \times 33 \times 1$ grid blocks of volume $3 \times 3 \times 3$ m³ each. A quarter of a 10-acre five-spot well pattern (i.e., CO₂ injector and oil producer) is set up for the reservoir model. Thus, the EOR and CCS performances are mainly governed by the displacement and sweep efficiencies. The total simulation period is 13 years (2007–2020), beginning with 3 years of waterflooding followed by 10 years of WAG, as shown schematically in Figure 2. The WAG consists of five cycles, in each of which water and gas are injected sequentially. Four WAG model simulation cases are analyzed, namely: 100% CO₂ + 0% CH₄ (Case 1), 90% CO₂ + 10% CH₄ (Case 2), 80% CO₂ + 20% CH₄ (Case 3), and 70% CO₂ + 30% CH₄ (Case 4). The gas injection rate for each case is a constant 2265 m³/day under surface conditions to determine the effects of CO₂ and CH₄ compressibility upon EOR performance while excluding the effect of any difference in injection rate. The initial conditions for the reservoir model are presented in Table 4. Thus, the producing bottom hole pressure is fixed at 13,789 kPa, while the initial reservoir pressure and temperature are computed on the basis of hydrostatic and geothermal gradients.

**Figure 2.** Schematic diagram of the water alternating gas (WAG) injection model.**Table 4.** Initial and operating conditions used for the reservoir simulation.

Parameters	Values
Depth (m)	2811
Initial reservoir pressure (kPa)	27,579
Reservoir temperature (°C)	63
Permeability (m ²)	1.0×10^{-13}
Porosity (%)	0.25
Initial oil saturation, S_o (fraction)	0.7
Connate water saturation, S_w (fraction)	0.3
Producing bottom hole pressure (kPa)	13,789

The decrease in displacement efficiency due to CO₂-CH₄ co-injection is described in terms of the IFT between the displacing and displaced fluids in the middle of the reservoir (grid block co-ordinates (17, 17, 1)) during the 13-year WAG in Figure 3. Due to the lower molecular weight of CH₄ compared to CO₂, the addition of CH₄ makes the displacing fluid lighter and the IFT of the gas mixture higher compared to that of Case 1, as indicated in Figure 3a. In addition, the IFT after the multiple contact with the initial oil (2010–2011) is examined more closely in Figure 3b. Here, Case 1 gives the lowest IFT value of 0.08 mN/m between the CO₂ and reservoir oil, while Cases 2, 3, and 4 give 225%, 588%, and 1000% higher values of 0.26, 0.55, and 0.88 mN/m, respectively.

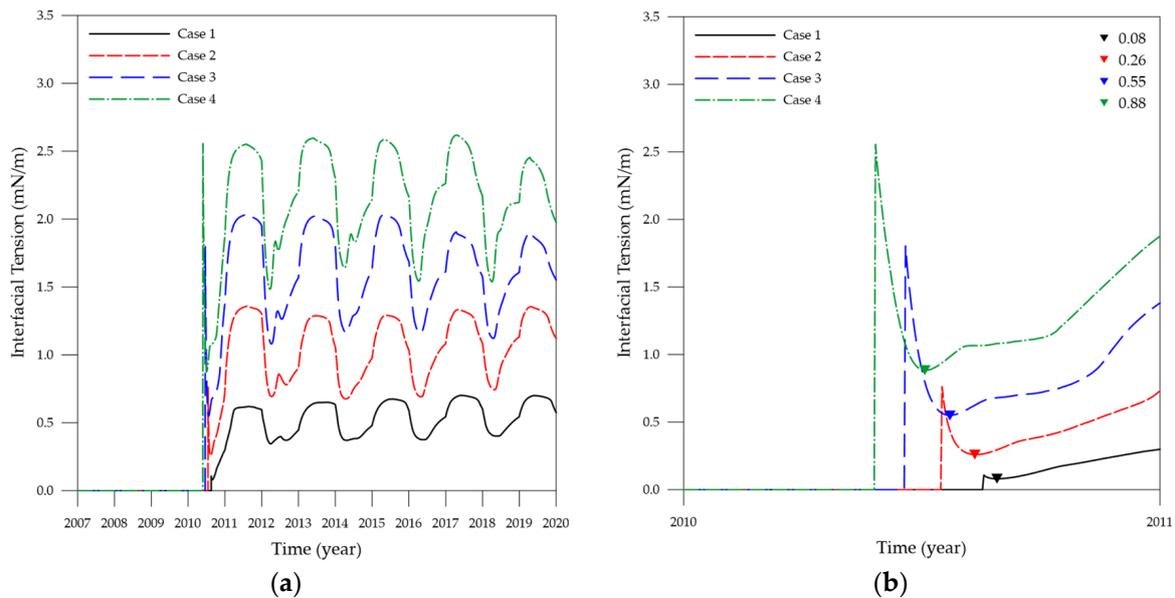


Figure 3. Interfacial tension (IFT) with CH₄ addition into the CO₂ stream during the WAG process under reservoir conditions ($T = 63\text{ }^{\circ}\text{C}$) for (a) 2007–2020, (b) 2010–2011.

Meanwhile, the decrease in displacement efficiency due to CO₂-CH₄ co-injection is described in terms of the 2D change in oil viscosity when 0.15 PV of gas is injected in Figure 4. The blue swept area in Figure 4a indicates that the injected fluids make maximum contact with the reservoir oil in Case 1, and that the minimum oil viscosity in this Case is 0.46 mPa·s. When 20% mole fraction of CH₄ is added into the CO₂ injection stream (Case 3), the deep blue region of Figure 4a changes to the light blue area of Figure 4b, indicating a 23.9% increase in the oil viscosity from 0.46 mPa·s to 0.57 mPa·s. The injected gas displaces the light and intermediate oil components from the initial oil, thereby increasing the oil viscosity after the multiple contact. For Case 1, the oil viscosity near the gas injector is zero because the oil is displaced by the high injection pressure and is miscible with the CO₂. In addition, Figure 4 shows that the injection gas front in Case 3 is more convex than that in Case 1. This is because less gas is acting as a solvent to reduce the oil viscosity, while the fraction of injected gas that does not come into contact with the oil creates a gas channel that leads to early breakthrough of produced gas, as indicated in Figure 5.

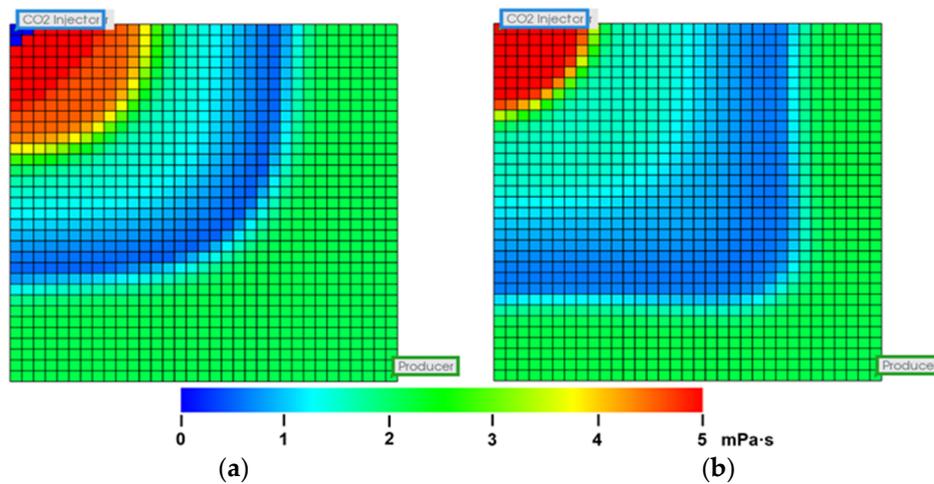


Figure 4. WAG models of oil viscosity at 0.15 PV injection for (a) Case 1, (b) Case 3.

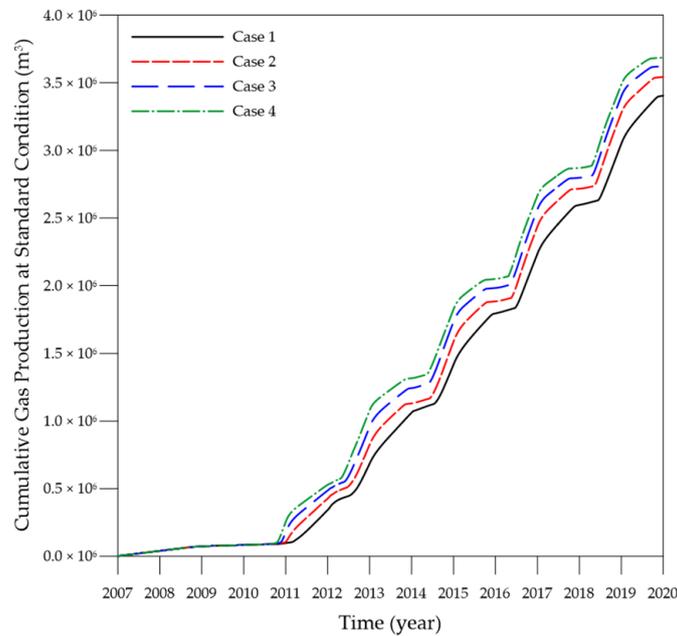


Figure 5. Cumulative gas production obtained from the four CO₂-CH₄ WAG cases under standard conditions.

The cumulative gas injection under the reservoir condition obtained from the four CO₂-CH₄ WAG cases is indicated in Figure 6. Note that although the gas injection rate at the surface is constant, the volume occupied by gas differs in each case because CH₄ is less compressible than CO₂; hence, the more CH₄ is added, the higher the gas injection rate at the reservoir (Jin et al., 2017). In addition, the average gas saturation in each of the four cases for the ten-year WAG period is indicated in Figure 7. In the first WAG cycle (2010–2012), Case 1 displays the lowest average gas saturation, while Cases 2 to 4 indicate that the average gas saturation increases with increasing addition of CH₄ to the gas stream as CH₄ occupies more reservoir pore volume than does CO₂. Interestingly, this trend is reversed in the subsequent WAG cycles due to the poor sweep efficiency resulting from the CH₄ addition, so that the average gas saturation eventually becomes the lowest for Case 4 by the end of the final WAG cycle (2019). Meanwhile, the average reservoir pressure obtained from the four CO₂-CH₄ WAG cases is indicated in Figure 8, where the greater pore occupation by CH₄ is seen to increase the average reservoir pressure due to the lower compressibility of CH₄ relative to CO₂. As a result, the co-injection of CO₂-CH₄ generates higher oil recovery than the pure CO₂ WAG during the early stages of WAG

(2010–2012), but reduces the overall oil recovery at the end of the WAG process, as indicated in Figure 9. This is because the effects of displacement and reduction in sweep efficiency become more dominant than that of compressibility as the WAG proceeds.

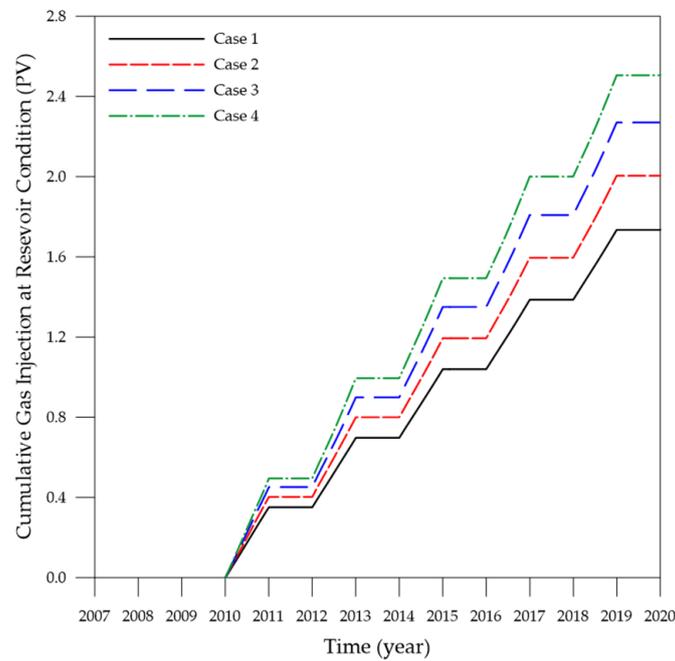


Figure 6. Cumulative gas injection obtained from the four CO₂-CH₄ WAG cases at the reservoir condition (T = 63 °C).

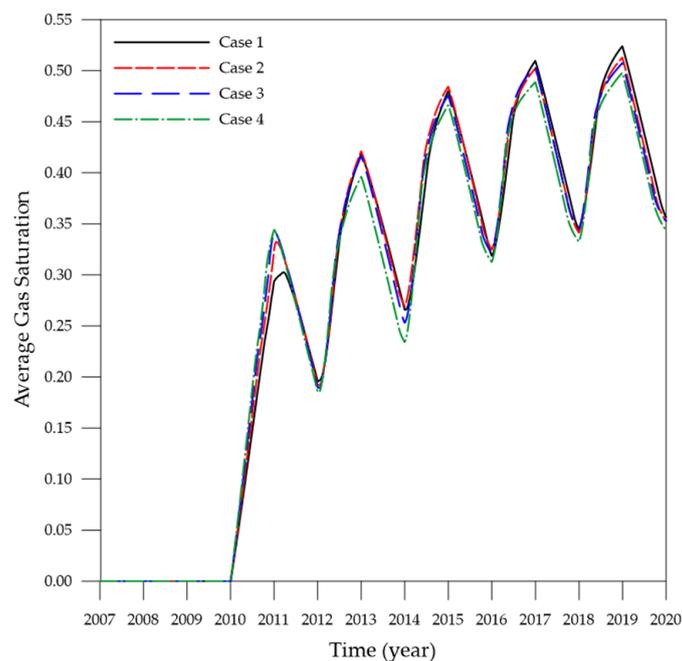


Figure 7. Average gas saturation obtained from the four CO₂-CH₄ WAG cases.

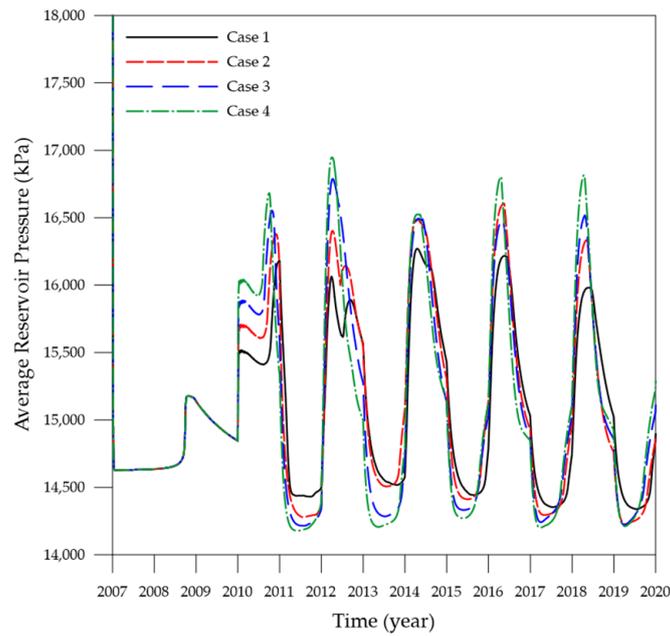


Figure 8. Average reservoir pressure obtained from the four CO₂-CH₄ WAG cases.

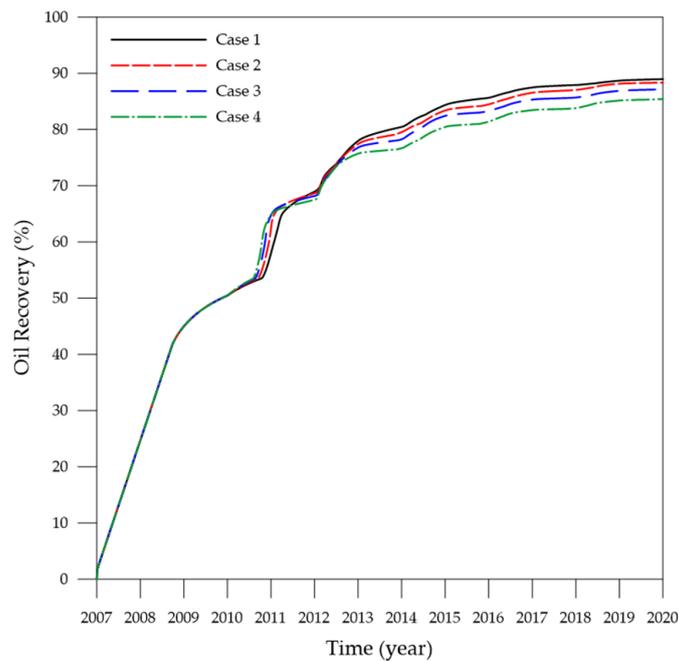


Figure 9. Oil recovery factor obtained from the four CO₂-CH₄ WAG cases.

3.3. Effects of CH₄ Injection on Carbon Storage Efficiency

As indicated in Figure 7, the addition of CH₄ to the CO₂ stream reduces the WAG sweep efficiency and gas saturation, thus decreasing the S_{gm} (Equation (4)) to lower the trapped gas saturation, S_{gr} . As a result, the residual trapped CO₂ by hysteresis (Figure 10) is seen to decrease as the ratio of CH₄ to CO₂ in the gas stream increases. In addition, the amount of solubility-trapped CO₂ decreases as the concentration of CH₄ increases, as indicated in Figure 11. However, this decrease is primarily due to the reduced volume of injected CO₂ and does not mean that the addition of CH₄ lowers the performance of solubility trapping. As mentioned in Section 3.2., the injected total gas rate is set to a constant of 2,265 m³/day, so that the amount of injected CO₂ decreases with increasing CH₄ addition.

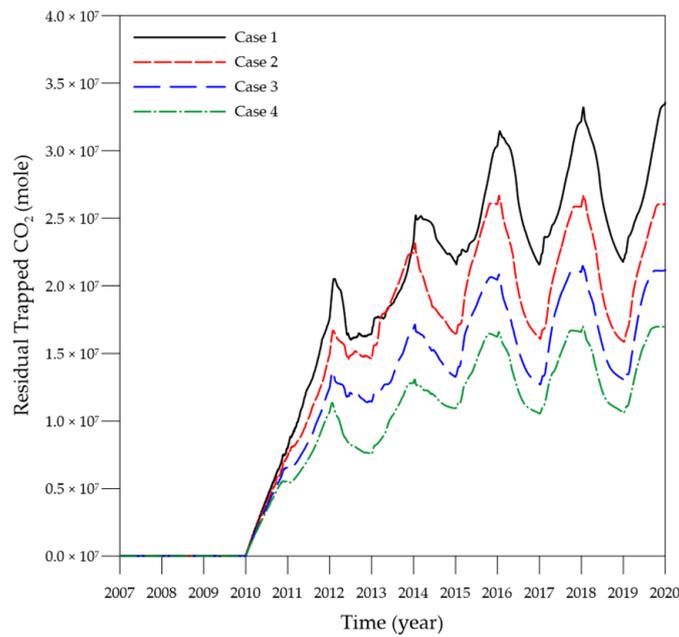


Figure 10. Residual CO₂ trapped by hysteresis obtained from the four CO₂-CH₄ WAG cases.

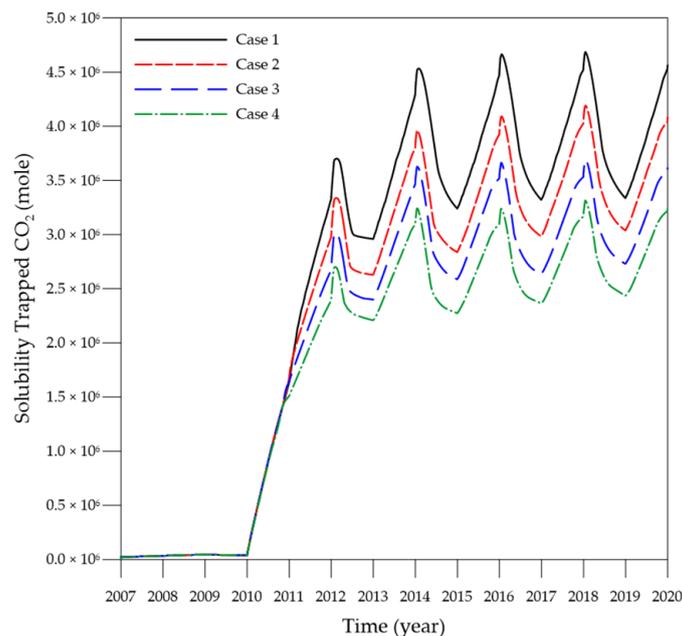


Figure 11. Solubility-trapped CO₂ obtained from the four CO₂-CH₄ WAG cases.

The contributions of the residual trapping and solubility trapping mechanisms to geological carbon sequestration is examined in Figure 12 by comparing the mole proportions of injected and remaining CO₂. Note that movable CO₂ also has the potential to be trapped over time. Thus, compared to Case 1, the residual trapping performances of Cases 2, 3, and 4 are seen to decrease by 13.2%, 20.5%, and 27.4% respectively, due to the lower hysteresis effect and gas saturation. By contrast, the solubility trapping efficiencies remain relatively constant as the amount of injected CO₂ is reduced with CH₄ addition. This is because the CO₂ solubility trapping is affected not only by gas saturation but also by reservoir pressure. Since the added CH₄ increases the reservoir pressure, as indicated in Figure 8, this balances out the negative effect of the reduced CO₂ injection, thereby resulting in the similar CO₂ solubility trapping performance. Meanwhile, the amount of movable CO₂ remaining in the reservoir decreases with increasing concentration of CH₄ due to the gas breakthrough effect.

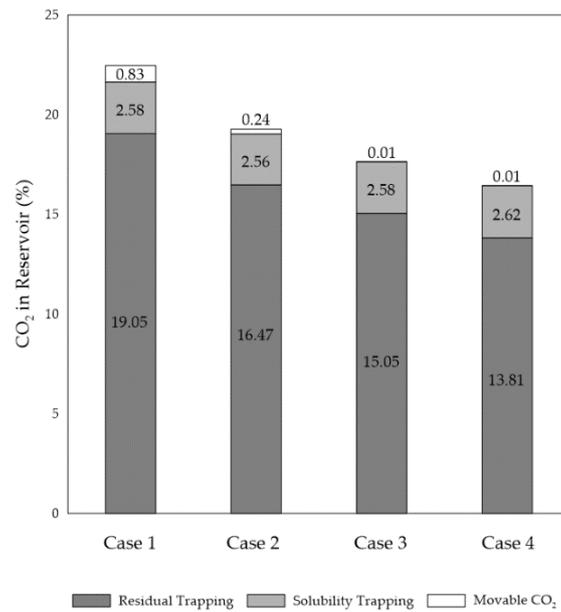


Figure 12. The proportion of CO₂ remaining in the reservoir relative to the injected volume of CO₂ for the four CO₂-CH₄ WAG cases depending on the trapping mechanisms.

Although the above results elucidate the aspect of CO₂ sequestration, it is also necessary to consider the contribution of CH₄ storage because the GWP of CH₄ is about 28 times that of CO₂. The GWP is an index of the relative amount of heat trapped by a unit mass of other GHGs compared to CO₂. In the present study, the GWP is transformed into the index per 10⁷ moles of GHG. GWP of CH₄ per 10⁷ moles is ten times higher than that of CO₂ with consideration for the molecular weight of each gas. In other words, the effect of 1 mole of CH₄ sequestration upon the prevention of global warming is the same as that of 10 moles of CO₂ sequestration. Thus, the relative amounts of trapped GHGs are presented in Figure 13, where 10⁷ moles of trapped CO₂ and CH₄ are quantified as 1 and 10, respectively. For Case 1, the net GWP of trapped gases is 3.94 – 2.13 = 1.81, under the assumption that CH₄ is only produced without re-injection into the reservoir. As the CH₄ concentration increases, the trapped GWPs for the co-injection cases are increased by 123%, 230%, and 313% respectively, compared with Case 1 due to the CH₄ sequestration effect in spite of the reduction in CH₄ storage.

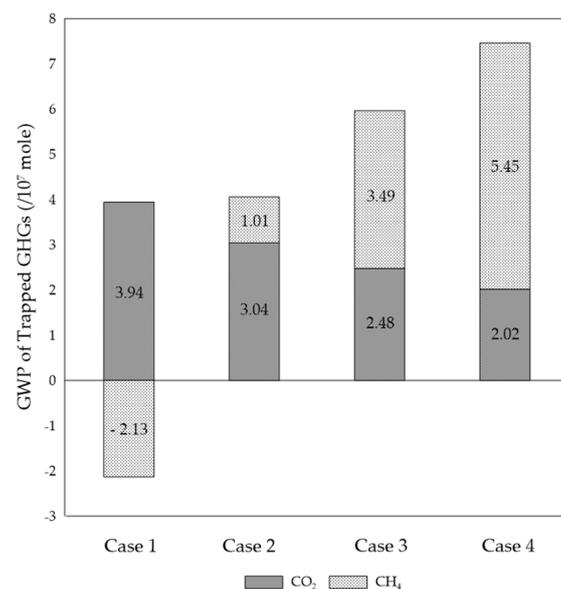


Figure 13. The GWP of trapped greenhouse gases obtained from the four CO₂-CH₄ WAG cases.

4. Discussions

This study investigated the effects of CO₂-CH₄ co-injection on CCS-EOR performance and mechanisms using the compositional 2D reservoir simulation. The 2D homogeneous plane model was designed in order to focus on the miscibility and sweep efficiency without gravity override during WAG simulations. We anticipate that the proposed compositional model can be extended to a three-dimensional (3D) heterogeneous model for real field applications. Adding CH₄ into the CO₂ stream may affect the vertical sweep efficiency, resulting in the change of the CCS-EOR performance because the density of CH₄ is much lighter than that of CO₂. Also, reservoirs are heterogeneous in reality. The effects of heterogeneity on the performance are under investigation as future works.

Moreover, it is essential for the technically, economically, and environmentally sustainable development of CO₂-EOR fields to analyze both oil recovery and carbon storage efficiencies in an integrated way. For an actual field application, the optimal CO₂-CH₄ injection design should be developed with consideration for economic factors, such as the volatile oil price, CO₂ and CH₄ purchase and recycle prices, operating costs, and tax credits for CCS. Ettehadtavakkol et al. [46] focused on the sensitivity of economic parameters with various WAG ratios during CCS-EOR, but no study has been conducted in the CO₂-CH₄ co-injection system to the best of our knowledge. Since the optimum operating conditions enhancing the performance of CCS-EOR depend on reservoir characteristics, it is necessary to develop a site-specific design based on economic analysis for the field application.

Gas injection changes the stability of asphaltene precipitation and deposition, and formation damages by asphaltene deposition affect CCS-EOR performance. The effects of asphaltene deposition on CCS-EOR in the CO₂ WAG process have been investigated in Cho et al. [19], while the effect of CH₄ addition has not been studied yet. We clarify that the CO₂-CH₄ co-injection model considering asphaltene deposition is being developed as our on-going work.

5. Conclusions

A compositional numerical simulation was conducted to investigate the effects of CH₄ additions upon the coupled CO₂-enhanced oil recovery (EOR) and carbon storage process. The oil properties were matched to the reference data from Weyburn W3 via the equation of state (EOS) parameter tuning. The minimum miscibility pressure (MMP) between the CO₂/CH₄ mixture and the reservoir oil was estimated using the multiple-mixing-cell method. Based on the fluid model, the three-phase hysteresis model and Henry's law were applied for accurate simulation of WAG injection under dynamic conditions. The following conclusions were drawn from this study.

Because adding CH₄ to the CO₂ stream increased the MMP, the interfacial tension (IFT) between the co-injected gases and the reservoir oil had a higher value than that of CO₂ alone. Further, the addition of CH₄ resulted in a less pronounced reduction in oil viscosity after multiple contacts with the gas stream, thus indicating the lower displacement efficiency. Since CH₄ is less compressible than CO₂, the CO₂/CH₄ mixture occupied more pore volume than CO₂ in the first WAG cycle, but the reduction in sweep efficiency due to CH₄ addition reversed this tendency in subsequent cycles. Hence, although the CH₄ addition resulted in a higher EOR performance in the early stages due to the compressibility effect, the EOR performance was subsequently reduced due to the lower displacement and sweep efficiencies. The diminished sweep efficiency due to CH₄ addition led, in turn, to a reduction in the residual trapping performance of CO₂. By contrast, the increased reservoir pressure acted to offset the lower sweep efficiency for CO₂ solubility trapping, thus maintaining the performance even with increasing amounts of CH₄ addition. Taking the global warming potentials (GWPs) of the respective gases into consideration, the overall carbon capture and storage (CCS) effects were improved by 123%, 230%, and 313% by the use of CH₄ to CO₂ ratios of 0.1, 0.2, and 0.3 respectively, compared to the use of CO₂ alone. In conclusion, the developed model demonstrates that CH₄ has the combined effect of reducing EOR performance but increasing CCS performance. The above results indicate the significance of the integrated analysis for accurate CO₂ sequestration in depleted or depleting hydrocarbon reservoirs under EOR.

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Nomenclature

α	Reduction exponent
$f_{i,o}$	Fugacity of the i -th component in the oil phase
$f_{i,g}$	Fugacity of the i -th component in the gas phase
$f_{i,w}$	Fugacity of the i -th component in the water phase
H_i^S	Henry's constant for the i -th component at the saturation pressure of water, MPa
k_{rg}^{drain}	Relative permeability of the gas during the secondary and following drainage processes
k_{rg}^{input}	Input relative permeability of gas
k_{rg}^{imb}	Relative permeability of gas imbibition process
n_c	Number of components
p	Reservoir pressure, MPa
p_c	Critical pressure, kPa
$p_{H_2O}^s$	Saturation pressure of water at temperature T, MPa
R	Gas constant
S_w^I	Water saturation at the start of the drainage process
S_g^{start}	Gas saturation at the start of the drainage process (end of previous imbibition)
S_{wi}	Initial water saturation
S_{gf}	Free gas saturation
S_g^{end}	Endpoint gas saturation of imbibition
S_{gc}	Critical gas saturation in the input relative permeability table
S_{gm}	Maximum gas saturation reached by drainage
$S_{g,max}$	Maximum gas saturation associated with the imbibition
S_{om}^{mod}	Modified minimum residual oil saturation
T_c	Critical temperature, K
T_{r,H_2O}	Reduced temperature of water
v_{CO_2}	Partial molar volume of CO ₂ at infinite dilution (cm ³ ·mol ⁻¹)

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