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## Abstract

During the past decade, enhanced oil recovery (EOR) by CO<sub>2</sub> in shale oils has received substantial attention. In shale oil reservoirs, CO<sub>2</sub> diffusion into the resident oil has been considered as the dominant interaction between the CO<sub>2</sub> in fractures and the oil in the matrices. CO<sub>2</sub> diffusion will lead to oil swelling and improvement in oil viscosity. However, despite two-way mass transfer during CO<sub>2</sub> EOR in conventional oil reservoirs, one-way mass transfer into shale oils saturated with live oils is controlled by an additional transport mechanism, which is the liberation of light oil components in the form of a gaseous new-phase. This *in-situ* gas formation could generate considerable swelling, which could improve the oil recovery significantly. This mechanism has been largely overlooked in the past. This study is aimed to better understand the role of this evolving gas phase in improving hydrocarbon recovery.

Taking account of Bakken shale oil reservoir data, numerical simulations were performed to identify efficiencies of EOR by CO<sub>2</sub> at the laboratory and field scales. Equation of state parameters between CO<sub>2</sub> and oil components were adjusted to optimize the calculations and a sensitivity analysis was performed to identify the role of gas formation and consequent EOR efficiencies. At the laboratory scale, *in-situ* gas formation can increase oil recovery by 20% depending on the amount of gas saturation. Also, the CO<sub>2</sub> storage capacity of the shale matrix can be enhanced by 25%, due to CO<sub>2</sub> trapping in the gas phase. At the field scale, an additional oil recovery of 9.1% could be attained, which is notably higher than previous studies where this gas evolution mechanism was ignored. Furthermore, the results suggest that a six-weeks huff period would be sufficient to achieve substantial EOR if this new mechanism is incorporated. On the other hand, the produced fluid in the early period was primarily composed of CO<sub>2</sub>, which would make it available for subsequent cycles. The produced gas of the well under CO<sub>2</sub> EOR was used in an adjacent well, which resulted in similar additional oil recovery and hence, impurities in CO<sub>2</sub> injection stream would not undermine efficiency of this EOR method. The results of this study, therefore, could potentially be used to substantially improve the evaluations of CO<sub>2</sub> EOR in liquid-rich shale reservoirs.

## 1. Introduction

Enhanced oil recovery (EOR) in unconventional liquid-rich reservoirs such as shale oils has become an emerging technology [1,2,3]. EOR for tight oils would have economic benefits as well as reducing the environmental impact. Increasing the oil recovery would improve the net present value (NPV) of a field, which would make it more profitable to operate. Also, improving the oil recovery in tight formations would reduce the need for re-fracking, which alleviate environmental concerns. In this work, we reveal a newly discovered mechanism for CO<sub>2</sub> EOR and CO<sub>2</sub> storage based on CO<sub>2</sub> diffusion into the oil and release of gas from the oil phase. We believe this process can (i) significantly improve the performance of EOR in fractured shales, (ii) accommodating significant capacity for CO<sub>2</sub> storage, (iii) improving the economy and (iv) reducing environmental impact.

Conventional production from shale oil reservoirs requires drilling a large number of wells, and then stimulating them by extended and multi-stage fracking, to have an economical production rate due to ultra-low permeability of shale reservoirs. However, each production well has a limited drainage radius and hence, exploitation of a reservoir necessitates drilling and fracking numerous wells. Also, the average life span of producing wells in shale oils is very short and hence, wells are frequently re-fracked, which would introduce higher levels of environmental concerns [4].

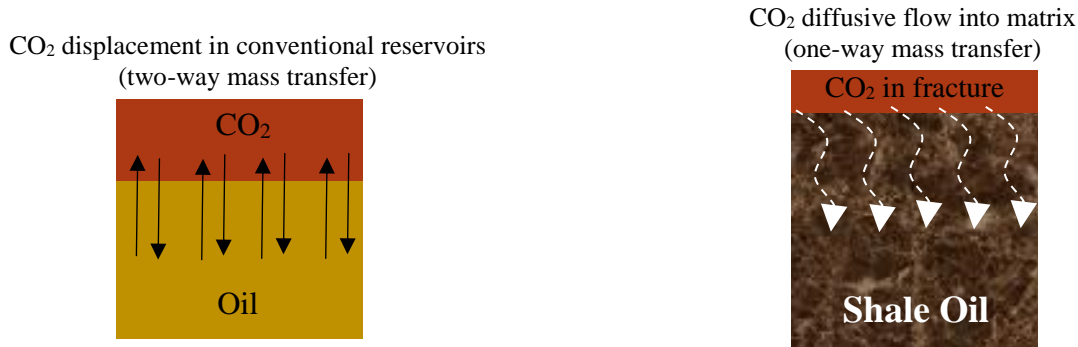
EOR in tight oils can be a technique way to improve the output of producing wells, which could reduce the need for re-fracking. Our analysis has indicated that an efficient CO<sub>2</sub> EOR would increase the oil recovery by 10%, which can be a reasonable replacement for re-fracking. However, physics and processes taking place during EOR in unconventional reservoirs may not be necessarily explained by the current perspectives. Here, through analogy with similar process, a new conceivable mechanism is studied, which would a gamechanger in EOR analysis for CO<sub>2</sub> injection scenarios. In addition to the impact on EOR, this new mechanism (to be explained in subsequent section) could increase the CO<sub>2</sub> storage capacity by 30% due to transfer of CO<sub>2</sub> into the gaseous phase. Therefore, an accurate analysis of CO<sub>2</sub> EOR technique is needed to evaluate feasibility of improving well efficiencies, which would also alleviate environmental consequences. In this work, details and significance of a new mechanism would be studied, which would predominantly control the efficiency of CO<sub>2</sub> EOR and CO<sub>2</sub> storage in shale oils. Using numerical modelling, a new insight on CO<sub>2</sub> EOR in shale and tight oil formations will be discussed. It has been observed that on-way CO<sub>2</sub> diffusion into live oil can liberate light hydrocarbon components leading to in-situ gas liberation. The similarity between processes under one-way mass transfer would postulate occurrence of this mechanism in shale oil reservoirs where CO<sub>2</sub> transport would be under one-way diffusion from fracture into matrices. Therefore, having utilized pore-scale observations in analogous processes, the importance of this new mechanism has been investigated using numerical simulation. The results of this study can be a game-changer in the evaluation of CO<sub>2</sub> EOR in fractured shale oil reservoirs.

### 1.1. Theoretical background

Based on the knowledge built on an analogous physical processes (i.e., under carbonated water injection), a new mechanism is conceivable to take place during CO<sub>2</sub> diffusion into shale oil matrices. The new mechanism will consolidate our understanding about this process and would change perception of stakeholders about CO<sub>2</sub> storage and EOR in tight reservoirs. It should be noted that, the analogy (similarity) in one-way mass transfer in carbonated water injection has only been considered for explaining the process of this new mechanism, i.e. gas liberation. This work is about injection of gaseous CO<sub>2</sub> injection *not* carbonated water injection.

Despite of two-way mass transfer during CO<sub>2</sub> EOR in conventional oil reservoirs as it is called condensing/vaporizing, CO<sub>2</sub> diffusion into oil-containing matrices would create a one-way mass transfer in shale oils, i.e. CO<sub>2</sub> dissolution and diffusive advancement. Figure 1 illustrates schematically the

difference in CO<sub>2</sub> transport in conventional and unconventional (shale oil) reservoirs. In shale oil reservoirs, once CO<sub>2</sub> is injected into the fracture, the diffusion of CO<sub>2</sub> through the oil would make the oil acting as a membrane allowing CO<sub>2</sub> to penetrate into the matrix. Therefore, the oil away from the fracture (not in direct contact with gaseous CO<sub>2</sub> in the fracture) would interact with the diffused CO<sub>2</sub> unlike conventional oil reservoirs where CO<sub>2</sub> is in direct contact with the oil in the invaded pores. Hence, it can be postulated that primary CO<sub>2</sub> transport is under what can be called as one-way mass transfer.



**Figure 1: Schematic illustration of the fundamental differences between conventional CO<sub>2</sub> displacement (left hand side) and CO<sub>2</sub> diffusion into shale oil matrices (right hand side). In CO<sub>2</sub> displacement, gaseous CO<sub>2</sub> is in direct contact with the oil leading to two-way mass transfer. However, in the one-way CO<sub>2</sub> diffusion into shale oil, the oil away from the fracture can not have direct contact with the CO<sub>2</sub> stream.**

This one-way mass transfer of CO<sub>2</sub> into the matrices is analogous to the processes taking place during carbonated water injection or CO<sub>2</sub> diffusion into water-shielded oil where CO<sub>2</sub> would be transferred from the injected water into the resident oil [5,6]. It has been recently reported that, in live oils with solution gas, one-way mass transfer of CO<sub>2</sub> would result in liberation of light components in the form of a gaseous new-phase [7,8]. Figure 2 illustrates the formation and growth of the new gaseous phase (digitally coloured yellow) during carbonated water injection [7]. This *in-situ* gas formation could favourably generate a considerable level of swellings, which could improve the oil recovery significantly [7,9]. Also, this new gas-phase would reduce the residual oil saturation significantly [7]. Furthermore, it has been demonstrated that, this liberated gas would stay immobile up to high critical gas saturation. The *in-situ* gas phase would tend to be immobile until it grows beyond 15% of gas saturation, which is a significant immobile (or critical) gas saturation [6]. The key factor for this important process to occur is the dissolved light to intermediate components in the live oil. In other words, during CO<sub>2</sub> injection, the presence of methane, ethane, and propane can lead to triggering of *in-situ* gas liberation. These essential components can be found substantially in live oils saturating shale oil reservoirs. In fact, most shale oil reservoirs would contain light oils [2], which can facilitate this process markedly. Based on the analogy of CO<sub>2</sub> behaviour (transfer) in carbonated water injection and shale oil reservoirs, it is plausible to postulate that CO<sub>2</sub> diffusion into the matrices would liberate the light components of shale oil, which would create significant additional swelling.

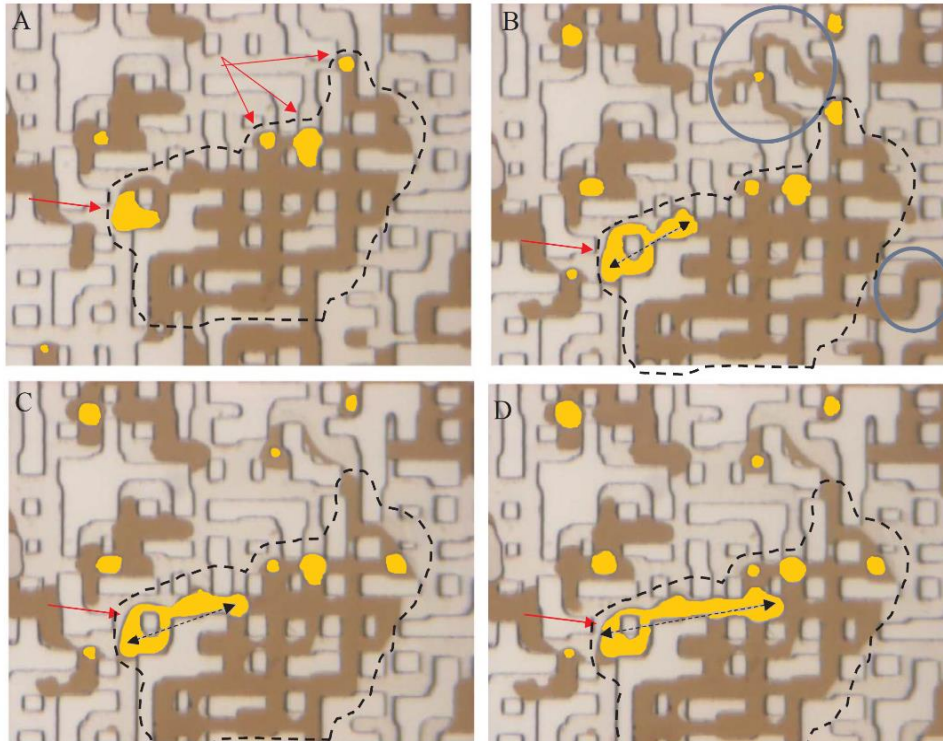


Figure 2: A sequence (A to D) of pore-scale observations of in-situ formation and growth of gas phase during carbonated water injection. Red arrows points to the gas phases formed (gas phase coloured yellow digitally). Highly magnified image on the upper left hand side show the micromodel after 2 hours of one-way mass transfer of  $\text{CO}_2$ . Growth and expansion of the gas phase within the oil ganglion is significant after two hours of carbonated water injection in image in lower right hand side [7].

Figure 3 represents the process of gas liberation inside matrices as  $\text{CO}_2$  is being injected into the fracture. Lack of practical understanding about the role of this pore-scale mechanism would misrepresent efficacies of  $\text{CO}_2$  EOR and  $\text{CO}_2$  storage in tight formations. In the previous studies, either this mechanism has not been captured or an oil without solution gas was used. For modelling analysis, it should be pointed out that another approach needs to be adopted to capture this mechanism. In other words, conventional parameters for equation-of-state (EOS) could not be able to capture this mechanism (which has been directly observed in numerous experiments). Therefore, a more representative set of parameters for EOS are required to capture this mechanism. In this modelling work, we have aimed to demonstrate the importance of this pore-scale mechanism during  $\text{CO}_2$  injection in shale oil reservoirs.

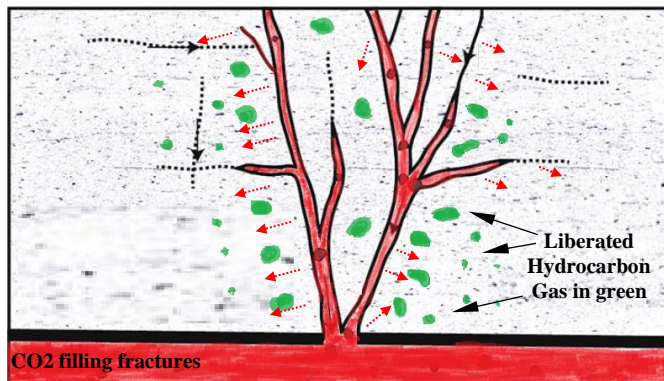
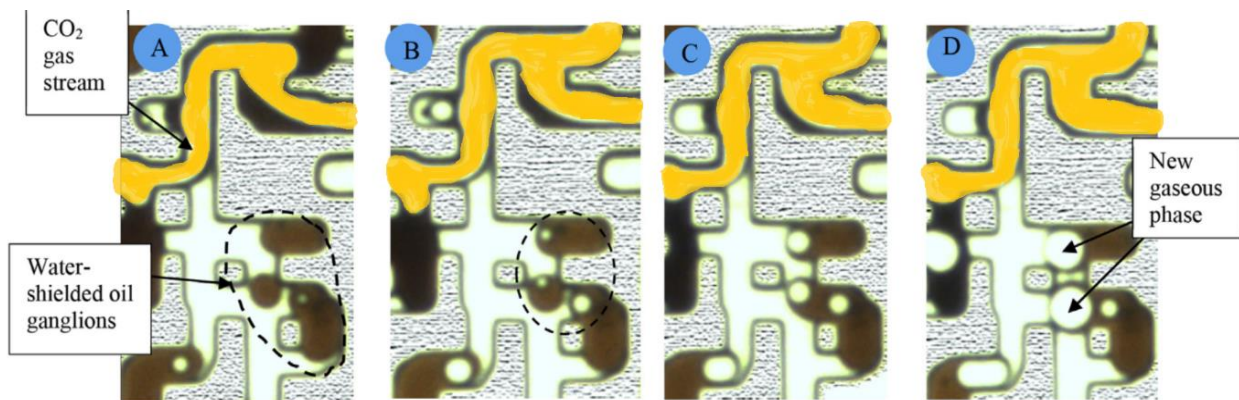


Figure 3: Schematic illustration of  $\text{CO}_2$  diffusion from hydraulic fractures into the matrix, which would lead to liberation of gas phase (digitally coloured green).

## 1.2. Experimental evidence

In the above section, the analogy and concepts of this new mechanism were explained to highlight the differences between conventional views on CO<sub>2</sub> injection (displacement) compared with the CO<sub>2</sub> transport in shale and tight formations where CO<sub>2</sub> diffusion is the prevailing transport process. However, more experimental evidence is required to verify whether this mechanism will occur during gaseous CO<sub>2</sub> injection. Figure 4 illustrates the pore-scale events occurring during CO<sub>2</sub> injection using a live oil saturated with methane [10]. The CO<sub>2</sub> stream was digitally coloured yellow. The images taken from the live oil away from the CO<sub>2</sub> stream (which was shielded with resident water) can indicate how one-way CO<sub>2</sub> diffusion through the water can trigger in-situ liberation of the shielded oil. These observations can be approximated to conditions of CO<sub>2</sub> injection in fractures interacting with the live oil inside matrices. As depicted in Figure 4, the CO<sub>2</sub> diffusion through the water could liberate the gas phase and it continued expanding during CO<sub>2</sub> injection. Therefore, CO<sub>2</sub> injection into systems under diffusive flow should be treated differently compared to conventional perceptions.



**Figure 4: Pore-scale observations of the impact of CO<sub>2</sub> transfer through the water layer, which led to gas phase liberation and growth. This can be very similar to CO<sub>2</sub> diffusion from fracture to shale oil matrices, where the oil in matrices would not have direct contact with the CO<sub>2</sub> in the fracture [10].**

The in-situ release of light hydrocarbons would lead to a significant degree of swelling owing to the fact that the gas phase would stay immobile. This additional swelling would boost up energies controlling the oil production. Since the extent of gas formation is primarily controlled by gas oil ratio, it can be inferred that shale oils would be a candidate for this mechanism as shale oils are highly rich in light and intermediate hydrocarbons. To quantify the behaviour of the liberated gas, a series of phase behaviour experiments were performed replicating the one-way mass transfer of CO<sub>2</sub> during carbonated water injection where, the composition of the liberated gas was analysed and total swelling factor was measured [8]. Figure 5 depicts gas composition and total swelling factor in multiple contacts between live oil and CO<sub>2</sub>-rich brine. Although the gas phase is composed of methane in the beginning, it can be observed that, this in-situ gas phase would have significant concentrations of CO<sub>2</sub> under high pressure as CO<sub>2</sub> transfer continued. CO<sub>2</sub> concentration in the gaseous phase would reach to around 80%. In terms of total swelling factor (i.e. oil+gas volume), the hydrocarbon phase can be expanded by 3 folds, which is significantly higher than that of conventional swelling factors used for CO<sub>2</sub> injection in conventional reservoirs [10].

Another implication of this new mechanism is the additional capacity for CO<sub>2</sub> storage in shale oils. Substantial portion of the in-situ gas phase would be composed of CO<sub>2</sub> (80% in Figure 5). Also, it has been demonstrated that, this in-situ gas phase would tend to be immobile until it grows beyond 15% of gas saturation, which is a significant immobile (or critical) gas saturation. These two factors (i.e. high CO<sub>2</sub> concentration in gas phase and high immobile gas saturation) could bring about notable degree of CO<sub>2</sub> storage capacity for CO<sub>2</sub> injection in shale formations. Therefore, not only significant additional oil recovery can be achieved, also notable amount of CO<sub>2</sub> storage can be attained. Therefore, in this study,

with aid of numerical modelling, the impact of this new mechanism was investigated to evaluate enhanced oil recovery and CO<sub>2</sub> storage capacity of CO<sub>2</sub> EOR in shale oil reservoirs.

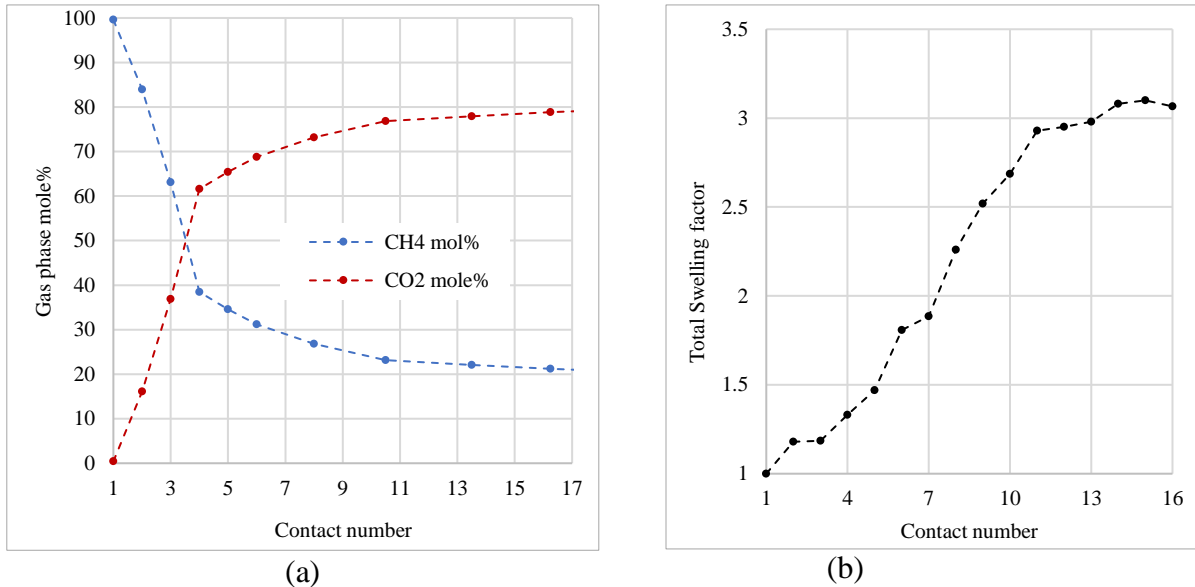


Figure 5: Quantitative characterisation of the composition of liberated gas and consequent total swelling (expansion factor) due to one-way mass transfer during carbonated water injection [8]. The liberated gas composed of methane in early stages and then, CO<sub>2</sub> was transferred into the gas phase leading to almost 80% of CO<sub>2</sub> in the gas phase. The total hydrocarbon volume (expansion factor = oil + gas volume divided by original oil volume) could swell up to 3.1 times.

## 2. Research Methodology

To evaluate the role of this new mechanism on the performance of CO<sub>2</sub> injection in shale and tight oil reservoirs, a series of numerical modelling exercises was performed to shed lights on the degree of misrepresentation of CO<sub>2</sub> efficiency for EOR and CO<sub>2</sub> storage in shale oils as reported in previous studies [3,11,12,13]. For the numerical modelling, two types of experiments were considered to simulate; (i) laboratory scale for diffusive flow of CO<sub>2</sub> into shale oil core and (ii) large-scale CO<sub>2</sub> huff-n-puff in a hydraulically fractured reservoir. For the simulations, CMG (oil reservoir simulation package) was used.

In the first type, the continuous flow of CO<sub>2</sub> through a fracture under constant pressure and temperature could simulate a diffusion-only flow of CO<sub>2</sub>. The boundary conditions were chosen in a way that injection and production of fluids would take place from fracture. This model would enable analysing the phenomena occurring in matrix grid cells away from the CO<sub>2</sub> stream in the fracture. Also, oil production would not be affected by other mechanisms such as gravity segregation. The core in the model was saturated with a live oil taken from middle Bakken shale oil reservoir. Also, the core properties were input from the Bakken shale oil reservoir [13].

For laboratory-scale simulation, two cases were performed using CMG-GEM simulator (a compositional reservoir simulator); (i) a base case where no gas liberation would happen as reported unrealistically in other simulations [13] and (ii) improved case where CO<sub>2</sub> interactions with hydrocarbon components were modified to take this new mechanism into consideration. Since this mechanism would be controlled by PVT properties, the EOS parameters that can trigger and control this mechanism are binary interaction coefficient between CO<sub>2</sub> and hydrocarbon components. In above sections, the strong analogy in one-way CO<sub>2</sub> transfer between CO<sub>2</sub> diffusion in shale oils and CO<sub>2</sub> diffusion in carbonated water injection. Therefore, for the improved case, the binary interaction coefficients proposed for carbonated water injection were incorporated for this modelling study [9,14]. In the absence of a representative set of experimental data performed on shale cores saturated with a live oil, the results of carbonated water injection can be the closest physic-based parameters for this simulation study.

For the large-scale simulations, a sector model (using CMG-GEM compositional simulator) with two horizontal wells was used. Each horizontal well was fractured with five planar fractures. The reservoir pressure and temperature were set to Bakken conditions. Also, the sector model was saturated with a live oil. The wells were undergone a pressure drawdown up to bubble point pressure of the oil, which prevents gas formation in the matrices during primary pressure drawdown stage and hence, gas liberation due to CO<sub>2</sub> transfer can be identified. Then, a series of CO<sub>2</sub> huff-n-puff cycles were performed between reservoir initial pressure (huff pressure) and oil original bubble point pressure (puff pressure). Like laboratory-scale modelling, two cases were sensitised; (i) using conventional parameters leading to no gas liberation and (ii) modified parameters triggering in-situ gas liberation. The outcome of this multi-scale modelling study can demonstrate the importance of this mechanism and the fact that, miss-representation of this mechanism can lead to significant under-estimation of efficiencies CO<sub>2</sub> EOR and CO<sub>2</sub> storage in shale and tight oil reservoirs. Also, the results can highlight the importance of using live oils in experiments performed for CO<sub>2</sub> EOR in shale and tight oils.

### 3. Numerical modelling results

#### 3.1. Laboratory-scale

To demonstrate the importance of this mechanism, a sensitivity analysis with aid of our current understanding of one-way CO<sub>2</sub> transfer was performed. Two cases have been numerically simulated where the conventional approach with no gas liberation is compared with a case with gas formation in a tight matrix. The model is a single matrix block topped with a fracture. The simulation model is initialized based on the available data published for Bakken shale oil reservoir [3,13]. CO<sub>2</sub> is injected into the fracture and to maintain pressure, a producing well was perforated at the fracture. Figure 6 illustrate the model with information used for initialization of the simulations. In the “Base” case where no gas formation would take place, all the information published for Bakken reservoir is used. In “Improved” case, the binary interaction coefficient (BIC) parameters were adjusted to values pertinent to fluid modelling of carbonated water injection in which light components were liberated [9,14]. Also, for gas-oil relative permeability (no mobile water exists in the model), a critical gas saturation of 15% was fixed in the relative permeability table as suggested by experimental observation of Mahzari et al and simulation results of Mesmari et al performed for carbonated water injection [7,9]. This new mechanism of in-situ gas liberation would resemble depressurisation process during depletion stage where gas starts to bubble within the oil phase. For the depressurisation process, a critical gas saturation can be conceivable higher than that of gas injection cases. Figure 7 illustrates schematically the experiment simulated numerically for one-way mass transfer. The results of gas saturation and pressure profile were plotted for a grid cell away from the main CO<sub>2</sub> stream in the fracture.

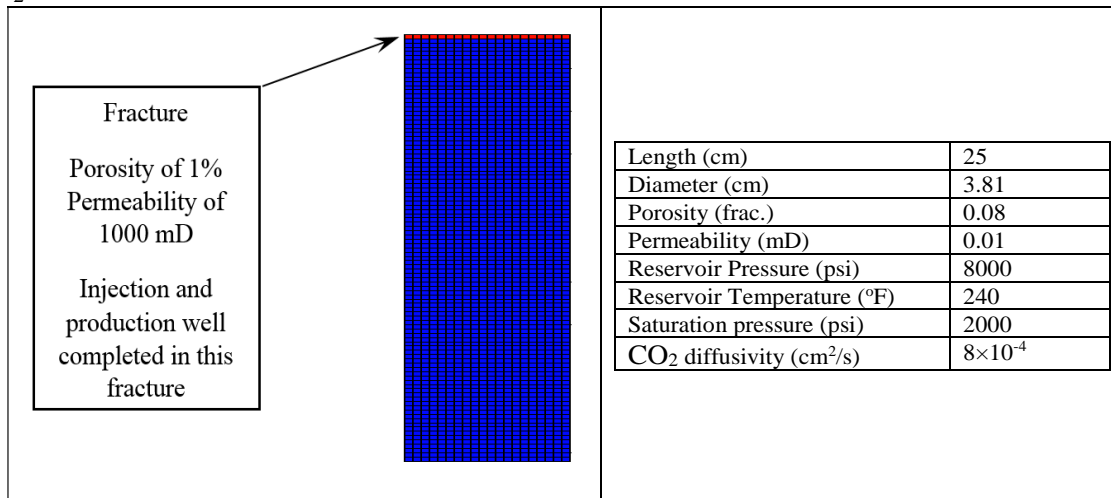


Figure 6: Fracture-matrix configuration in the laboratory model to represent diffusive-only transport of CO<sub>2</sub> into the shale core saturated with live oil. CO<sub>2</sub> is injected continuously at the top grid cells (in red) and produced from same grid cells. Rock and fluid properties were taken from Bakken shale oil reservoir [13].

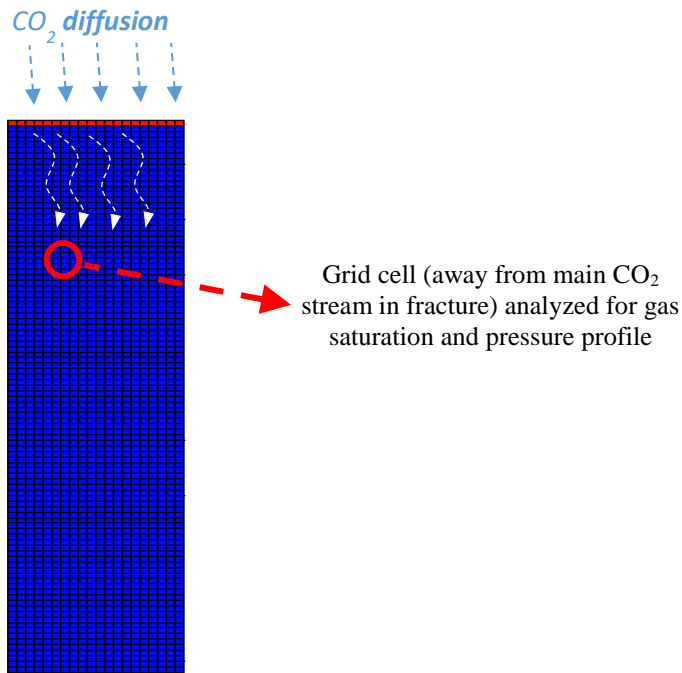


Figure 7: Diffusion of CO<sub>2</sub> in the matrix. 15<sup>th</sup> grid cell below the fracture was considered for analyses of gas saturation and pressure. The boundaries of the matrix (except top boundary) are sealed and hence, oil can only be produced from the top face through the fracture.

CO<sub>2</sub> was injected through the fracture with a very low rate to avoid pressurizing the system and allow a continuous dissolution of CO<sub>2</sub>. The producers operate under constant pressure mode maintaining the main CO<sub>2</sub> stream in the fracture, which ensure no displacement type of penetration of CO<sub>2</sub> into the matrix. Both injection and production points were perforated at the top grids, i.e. the fracture. Figure 8 illustrates the results of simulations for “Base” (conventional parameters) and “Improved” (parameters triggering gas liberation) cases. Figure 8 shows the profiles of pressure and gas saturation in a grid block  $x=5$  and  $z=85$ , which is 15 grids below the fracture. Figure 9 depicts average oil saturation in the core after three days. The gas saturation (Figure 8) of the improved case has reached 20% after 12 hours, which indicates an acceptable response time compared to normal huff and puff time-scales suggested for shale oils [3, 13, 15-17]. On the other hand, using conventional approach, no gas was formed in the grid block as shown with pink curve on Figure 8, which indicates the importance of using realistic parameters for EOS. One important consequence of in-situ gas formation can be manifested in pressure profiles. Evidently, before gas phase nucleation, red and blue curves in Figure 8 are on top of each other, however, as gas phase started to form, the pressure (or energy) generated in the “Improved” case (shown with blue curve) is higher than that of the “Base” case (shown with red curve), which can be directly linked to higher degree of swelling due to in-situ gas formation. This local increase (100 psi difference between two cases) in pressure can energise the matrix for pushing the oil towards to the fracture. Moreover, it can be inferred that the higher pressure may impact the micro-fractures due to local stress imposed on the matrix, which needs to be verified experimentally.

In terms of oil saturation profile, Figure 9 highlights that the average oil saturation in the matrix can be driven down by 25%, when the system could positively form in-situ gas phase. This reduction of oil saturation was replaced by the gas phase (or high-pressure CO<sub>2</sub>, which is a positive result for CO<sub>2</sub> storage). In the “Base” case, the oil saturation dropped by 3%. This significant difference between oil saturations can be directly translated into substantial improvement in oil recovery. The simulations results have demonstrated that in-situ gas formation can energise the matrix, which would lead to pushing the oil out.



It was shown that, as a consequence of in-situ gas liberation, the oil saturation was reduced efficiently by 25%, which was replaced by high gas saturation. The gas composition from fracture to the bottom the matrix could vary depending on the amount of diffused  $\text{CO}_2$ . However, the average  $\text{CO}_2$  composition of the gas phase was 69% weight percent. Therefore, there is a significant additional capacity for  $\text{CO}_2$  storage in the form of high pressure immobile gas within shale matrices. In other words, this new mechanism (in-situ gas liberation) would be a game-changer in evaluation of  $\text{CO}_2$  EOR and  $\text{CO}_2$  storage capacity in shale oil reservoirs and misrepresentation of this vital interaction would lead to underestimation of  $\text{CO}_2$  EOR and  $\text{CO}_2$  storage efficiencies in shale oils.

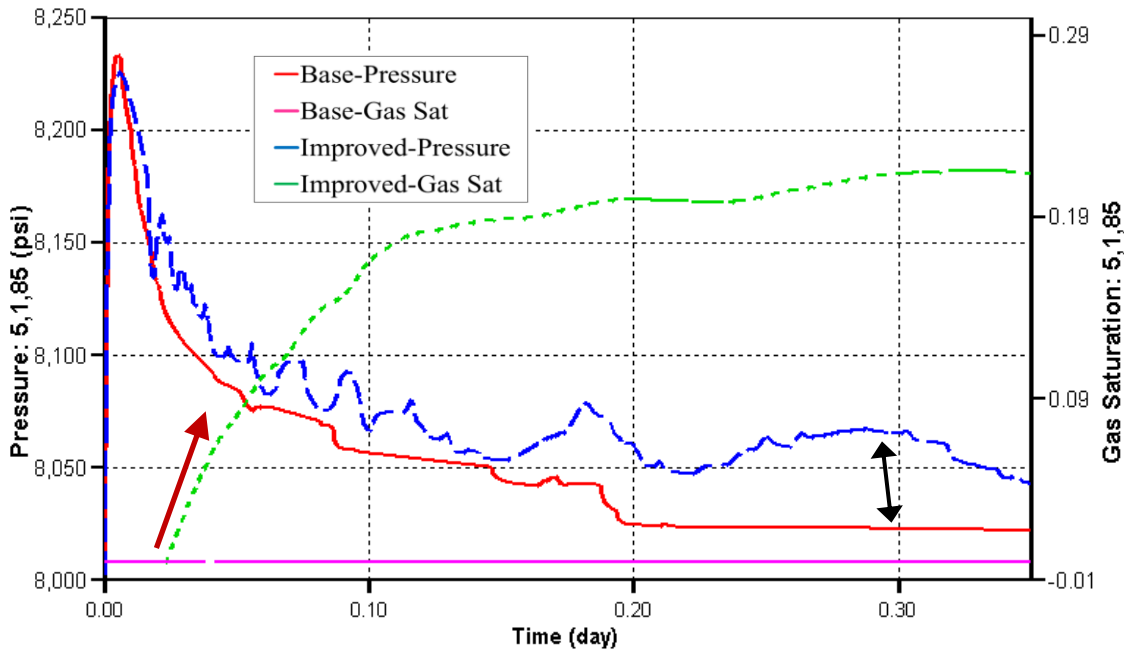


Figure 8: The profiles of pressure and gas saturation for “Base” and “Improved” case are plotted against time. The red arrow indicates the start of gas phase formation in the grid, which resulted in higher pressure (energy) created as highlighted with black arrow between pressure profiles of Base and Improved cases.

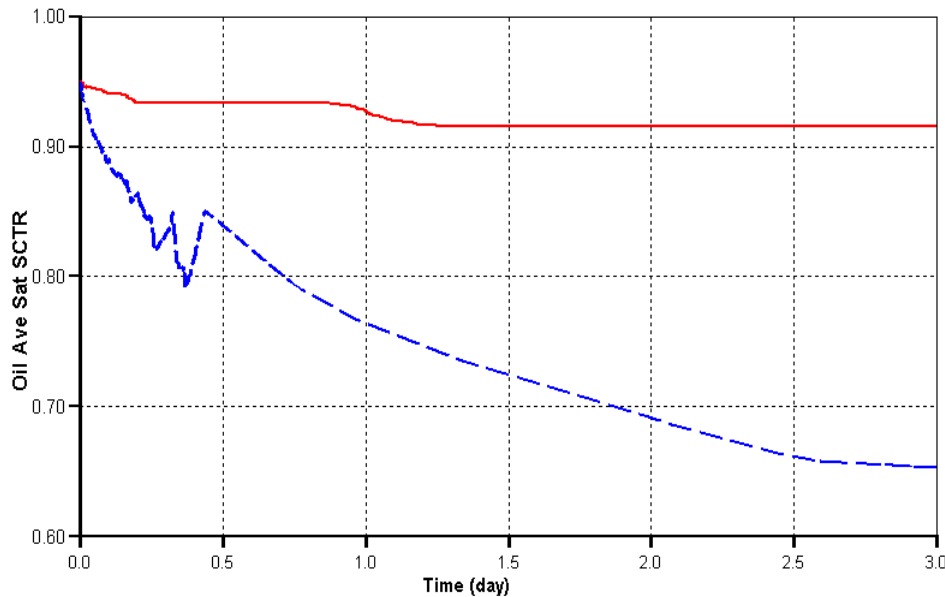


Figure 9: Average oil saturations in the matrix for the two cases are plotted against time. Blue curve is for the improved case with gas liberation mechanism and red curve shows the oil saturation with no gas liberation mechanism. Under gas liberation mechanism, significant reduction in oil saturation took place as the oil phase was replaced with the liberated gas.

### 3.2. Large-scale simulation (Sector Model)

Having identified the importance of the new mechanism of gas liberation in shale and tight rocks under CO<sub>2</sub> diffusion, a series of large-scale simulations was performed to evaluate the impact of in-situ gas liberation on EOR and CO<sub>2</sub> storage in hydraulically fractured shale oil reservoir. For that, a sector model with two horizontal wells was modelled as shown in Figure 10. Five planar hydraulic fractures were constructed for each well. The matrix properties are identical to what were used in laboratory-scale model assuming a homogeneous reservoir. The fracture permeability was 50 mD and grid cells around the hydraulic fractures were refined into smaller sizes to have better accuracies of the flow around the fractures. The sector model was run for 10 years under natural depletion with the wells operating under constant bottom hole pressure (bubble point pressure of the oil). Subsequently, the CO<sub>2</sub> injection was performed in a huff-n-puff mode with sequential cycles. In each cycle, CO<sub>2</sub> was injected to pressurize the wells up to initial reservoir pressure and after a certain soaking period, the bottom hole pressure was dropped to original bubble point pressure of the oil for drawdown periods.

Firstly, the impact of gas liberation mechanism was studied by comparing three simulation cases: (i) depletion for 30 years, (ii) 10 years of depletion followed by CO<sub>2</sub> huff-n-puff for 20 years with no gas liberation mechanism, and (iii) 10 years of depletion followed by CO<sub>2</sub> huff-n-puff for 20 years under gas liberation mechanism. For each cycle of huff-n-puff, the soaking period was 6 weeks for both CO<sub>2</sub> injection cases followed by 1.5 year of pressure drawdown. Figure 11 demonstrates the oil recovery profiles for these three cases. If the sector was operated under natural depletion, 9.9% of the original oil place would be produced. When CO<sub>2</sub> huff-n-puff cycles were performed with parameters leading to no in-situ gas liberation, 4.2% of additional oil recovery could be obtained. This amount of additional oil recovery is similar to previous studies [13], where the new mechanism was overlooked. Oil swelling and viscosity reduction were conventionally reported as the mechanisms behind 4.2% of additional oil recovery. Also, there has been another driving force for expelling oil out of the matrix, which is expansion of CO<sub>2</sub> forced into the matrices due to pressurisation. During pressurisation period, where CO<sub>2</sub> was pumped into the fractures, limited quantities of CO<sub>2</sub> would invade the matrices and hence, CO<sub>2</sub> expansion during drawdown period could lead to oil production.

However, for the third case, the EOS parameters were realistically modified to capture the gas liberation under one-way CO<sub>2</sub> mass transfer. If gas liberation mechanism is activated in the simulations, another parameter can come into play, i.e. CO<sub>2</sub> diffusion into the liberated gas. The CO<sub>2</sub> diffusion coefficient in gas phase was set to 10<sup>-3</sup> cm/s as suggested by [18]. As shown in Figure 11, the additional oil recovery of 9.3% was achieved. Hence, the EOR efficiency of CO<sub>2</sub> injection could be doubled under gas liberation mechanism. Therefore, overlooking this new mechanism can under-estimate markedly the EOR efficiency of CO<sub>2</sub> injection in shale and tight formations. To investigate the phenomenon behind the difference between cases with and without in-situ gas liberation, map of gas saturation distribution at end of huff-n-puff cycles are shown in Figure 12. When conventional binary interaction coefficients (BIC) were used, the gas phase was formed marginally in the vicinity of the wellbore due to pressurisation. However, when modified BICs values representing in-situ gas liberation were incorporated, the gas saturation could be noticeably increased in the areas away from the wellbore. It should be noted that the diffusive parameters (CO<sub>2</sub> diffusion coefficient in oil and gas phases) are identical in both cases. Therefore, using more representative parameters leading to gas liberation can cause gas bubbling within the resident oil in the areas where CO<sub>2</sub> could diffuse.

Beside the additional oil recovery, CO<sub>2</sub> huff-n-puff in the shale formation can be employed for CO<sub>2</sub> storage purposes. Given that numerous wells have been drilled for shale oil production, the synergy between enhanced oil recovery and CO<sub>2</sub> storage in each well can be viable. The simulation results presented in Figure 12 indicates that notable amount of gas was formed in the shale sector model. Provided that the in-situ liberated gas contained 63% of CO<sub>2</sub> (under pressure and temperature), an enhanced CO<sub>2</sub>

storage capacity was attained due to gas phase creation. This additional CO<sub>2</sub> storage would be on top of the CO<sub>2</sub> dissolved in the liquid oil phase. Based on simulation results with “no” gas liberation, only 9.1% of total CO<sub>2</sub> injected was stored after all huff-n-puff cycles. This amount of stored CO<sub>2</sub> can be attributed to CO<sub>2</sub> dissolution into the liquid oil phase and also, pumped CO<sub>2</sub> into the matrices. However, when gas liberation mechanism was in play, 26.9% of the injected CO<sub>2</sub> was stored permanently, which is almost three time higher. The enhanced CO<sub>2</sub> storage capacity was achieved by transfer of CO<sub>2</sub> into the gas phase in high concentration and also, improved CO<sub>2</sub> diffusion through the liberated gas phase.

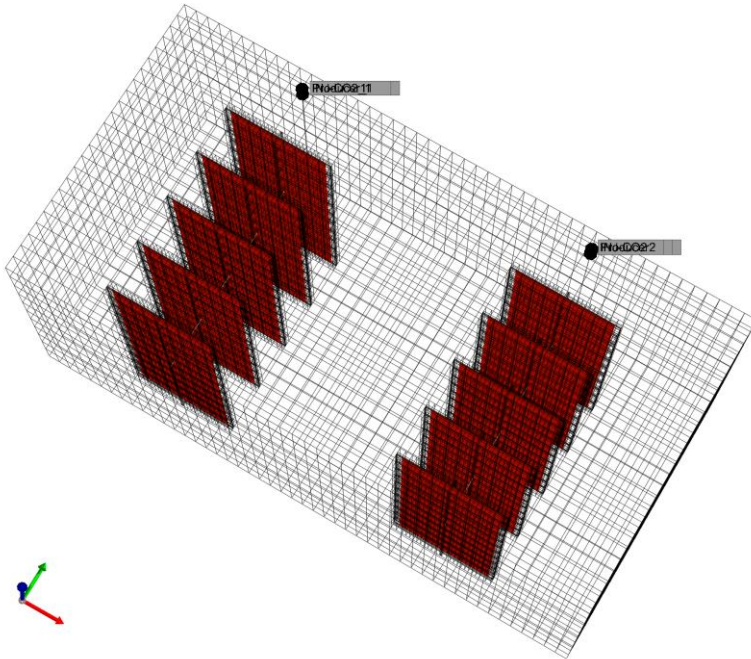


Figure 10: Field-scale (sector) model used for CO<sub>2</sub> EOR with two horizontal wells. The horizontal wells were fractured with five planar fractures. The rectangles in the model represent the fractures.

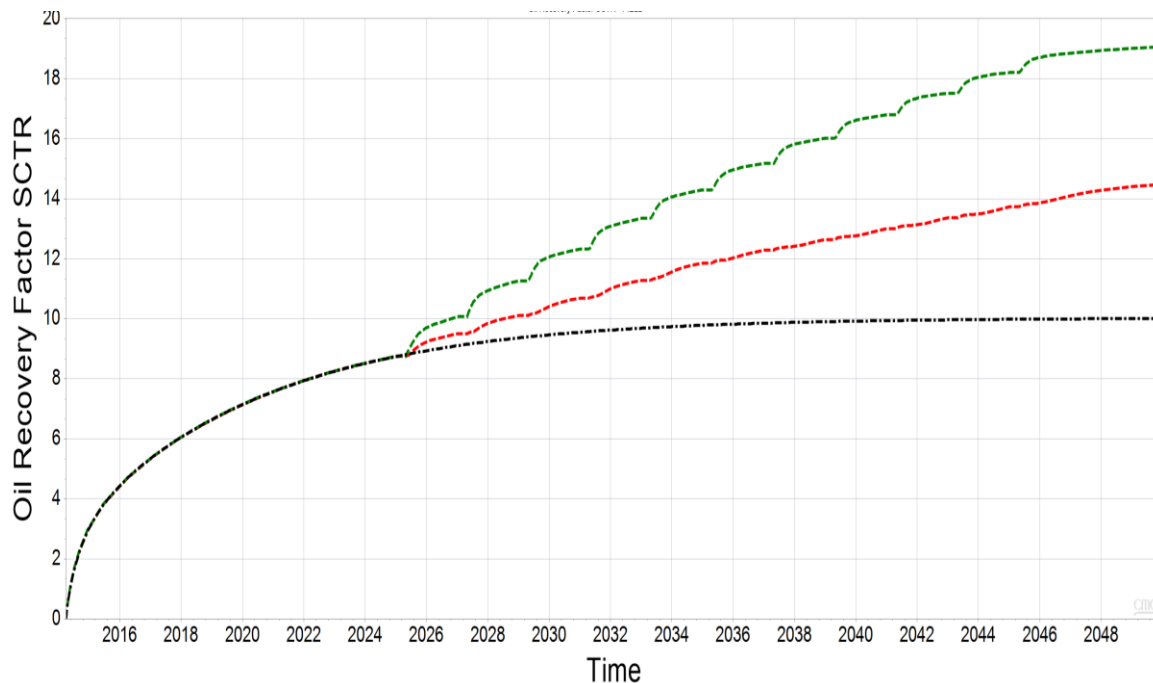


Figure 11: Cumulative oil recovery profiles for natural depletion (in black), CO<sub>2</sub> EOR with no gas liberation mechanism (in red), and CO<sub>2</sub> EOR with gas liberation mechanism (in green). Significant additional oil recovery can be achieved by CO<sub>2</sub> huff-n-puff if the EOS parameters are modified to capture the new mechanism.

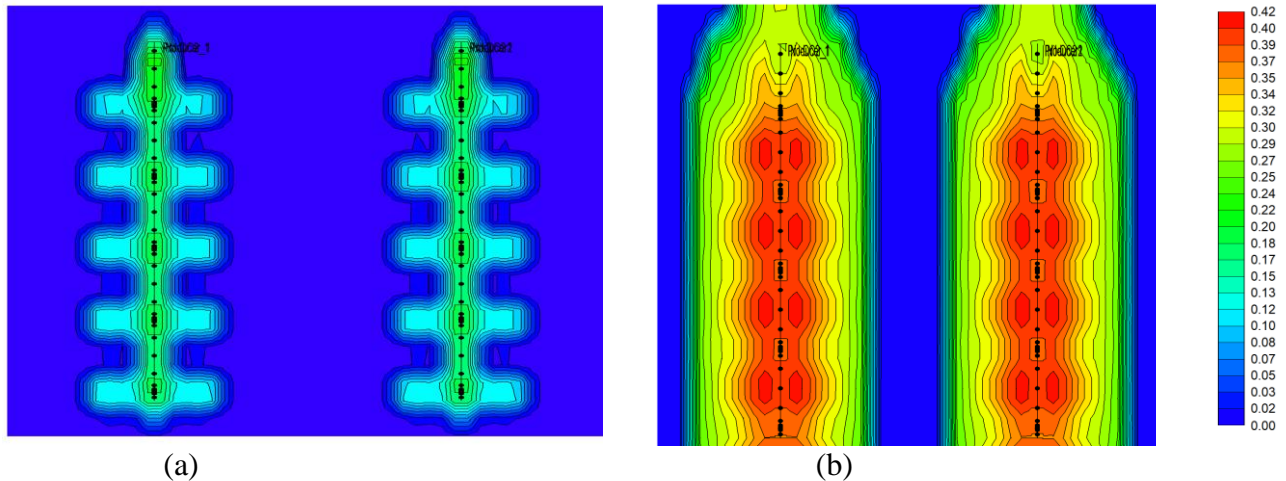


Figure 12: Gas saturation distribution at the end of CO<sub>2</sub> huff-n-puff for two cases: (a) with no gas liberation mechanism (left hand side image) and (b) with modified parameters to capture gas liberation (right hand side image). Significant amount of gas saturation was formed in the vicinity of the horizontal wells leading to significant additional oil recovery and CO<sub>2</sub> storage capacity.

Having identified the importance of gas liberation mechanism on the performance of CO<sub>2</sub> injection in shale and tight reservoirs, a series of sensitivity analysis can be performed to evaluate impact of operational parameters on CO<sub>2</sub> EOR in the system under gas liberation mechanism. For the sensitivity analyses, soaking time and injection gas composition were considered. Soaking time is one of the important constraints for implementing CO<sub>2</sub> EOR scenarios in shale and tight reservoirs. It would influence CO<sub>2</sub> penetration into the matrices due to diffusion. Figure 13 shows the effect of soaking time on the performance of CO<sub>2</sub> EOR. For these simulation, the total period of each huff-n-puff is identical. The EOS parameters were adjusted to capture gas liberation in these simulations. Soaking times of 20 days, 4 weeks, 6 weeks, and 3 months were considered. As can be seen in Figure 13, soaking time of 6 weeks would lead to additional oil recovery similar to that of 6 months soaking, which indicates the contribution of gas liberation to reduction of the soaking time.

Another important factor for large scale implementation of CO<sub>2</sub> EOR in shale oil reservoirs is the purity of injection CO<sub>2</sub> stream. For CO<sub>2</sub> injection in conventional oil reservoirs, where miscibility plays essential role in displacements, impurities (such as nitrogen and methane) in CO<sub>2</sub> stream would adversely affect the displacement efficiencies. However, in shale oil reservoirs, where CO<sub>2</sub> transport is controlled by diffusion, it is expected to observe different behaviour, as CO<sub>2</sub> has higher diffusion and dissolution characteristics (into oil) compared to methane. In our analysis of the simulation results, after each cycle of CO<sub>2</sub> huff-n-puff, the gas associated with the oil production has composition of 93% CO<sub>2</sub>. This high CO<sub>2</sub> concentration can be attributed to high CO<sub>2</sub> volume in the wellbore and also, in-situ liberation and trapping of light hydrocarbons (such as methane) in the shale matrices. One way of practical implementation of CO<sub>2</sub> EOR in shale oils is to collect the produced gas after one cycle of huff-n-puff and re-inject it into adjacent wells. Since EOR efficiencies are based on single well performance in shale oils, re-injection of collected gas in other well would make CO<sub>2</sub> EOR more economic and practically viable. Therefore, a sensitivity analysis on the impact of CO<sub>2</sub> impurity was performed. For these simulations, a gas injection stream with 90% CO<sub>2</sub> and 10% methane was considered for huff-n-puff process, which is even more contaminated that our analysis of the associated gas (i.e. 93%). Diffusion coefficient of methane in the oil phase was set at  $5 \times 10^{-6}$  cm/s.

Figure 14 demonstrates the results of simulations for three cases; (i) no CO<sub>2</sub> EOR, (ii) CO<sub>2</sub> EOR with 100% CO<sub>2</sub> stream in all cycles, and (iii) CO<sub>2</sub> EOR with 90% CO<sub>2</sub> composition in all cycles. As can be seen in Figure 14, the 10% impurity in the CO<sub>2</sub> stream has affected the performance of CO<sub>2</sub> EOR marginally. Indeed, collecting the associated gas and re-inject it into other wells would result in similar additional oil recovery (just 1% less compared to pure CO<sub>2</sub> injection). This behaviour can be attributed to

diffusion process where components would interact with the oil selectively based on their diffusion and dissolution parameters. In other words, the resident oil in shale matrices would act as a membrane that selectively allows  $\text{CO}_2$  to have more pronounced diffusion compared to methane. In other words, Oil would allow  $\text{CO}_2$  to diffuse and the methane would stay in the wellbore. Therefore, as opposed to conventional oil reservoirs where miscibility plays an essential role, the diffusive characteristics and gas liberation mechanism would control the efficiency of  $\text{CO}_2$  EOR.

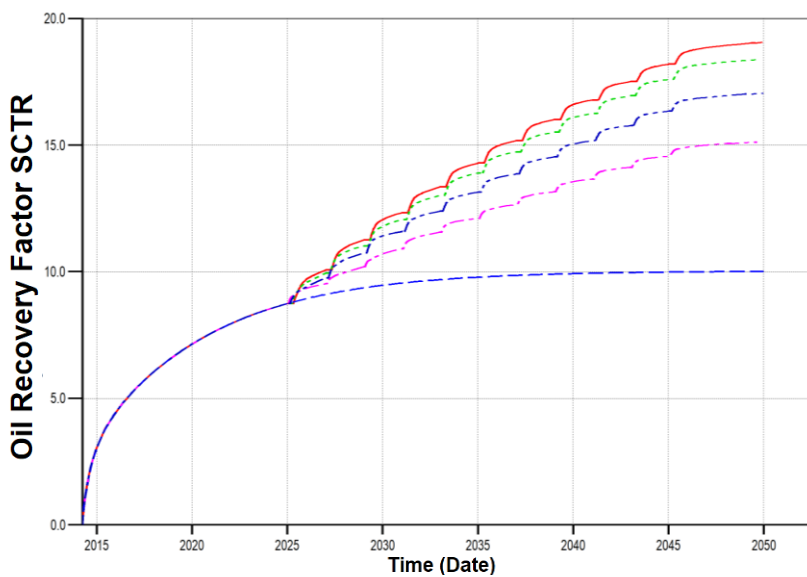


Figure 13: Effect of soaking time on the oil recovery profiles during  $\text{CO}_2$  huff-n-puff. Light blue curve is for natural depletion. Pink is for  $\text{CO}_2$  EOR with 20 days soaking time. Dark blue curve is for 4 weeks soaking time. Green curve is for 6 weeks soaking time. Red curve is for 6 months soaking time. 6 weeks of soaking time would be sufficient for optimum performance of  $\text{CO}_2$  huff-n-puff.

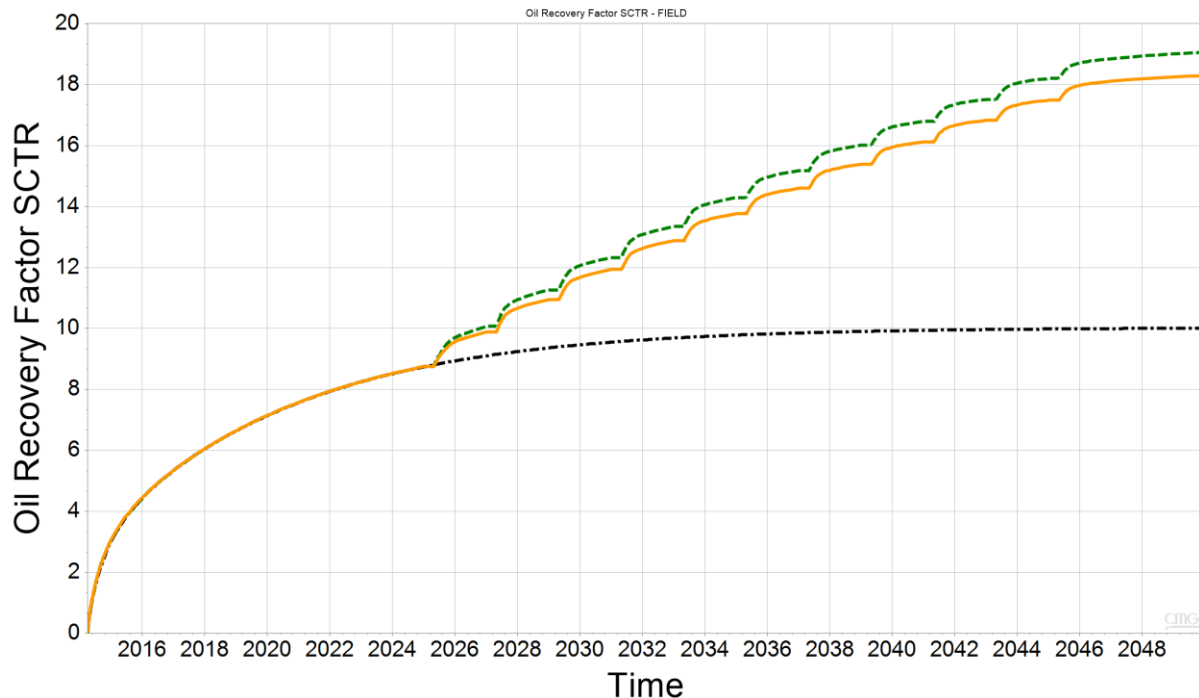


Figure 14: Effect of  $\text{CO}_2$  impurity on the oil recovery profiles. Black curve is for natural depletion. Yellow curve is for  $\text{CO}_2$  EOR with 90%  $\text{CO}_2$  and 10% methane injection stream. Green curve is for  $\text{CO}_2$  EOR with 100%  $\text{CO}_2$  stream. 10% impurity in the injection stream would not notably affect the performance of  $\text{CO}_2$  EOR.

In summary, from the experimental observations and the simulation results presented in this study, it can be inferred that the conventional approach to analyse the performance of  $\text{CO}_2$  EOR in shale oils

may be misleading. Occurrence of in-situ gas liberation mechanism during CO<sub>2</sub> diffusion can boost up the reservoir energy to push more oil out of the matrices. Gas liberation is a different process compared with extraction/vaporisation. To capture in-situ gas liberation, a modified set of EOS parameters should be used, which would result in expulsion of light hydrocarbon components as CO<sub>2</sub> diffuses into live oils. Therefore, conventional perception of extraction or vaporisation of hydrocarbon components by CO<sub>2</sub> may require to be revisited for systems under on-way mass transfer of CO<sub>2</sub>. Also, although saturating ultra-tight cores with live oils is very cumbersome and lengthy, it is essential to investigate CO<sub>2</sub> interactions with representative live oil under full reservoir conditions. In other words, laboratory experiments under reduced conditions may not be able to capture this new mechanism, i.e. gas liberation, and hence underestimating CO<sub>2</sub> EOR efficiencies. Thus, for CO<sub>2</sub> injection in shale and tight formations, there seems to have different mechanisms in play, which require a new paradigm for realistic evaluations and laboratory experiments.

#### **4. Conclusions**

In this work, with aid of previous experimental findings observed in analogous processes, the new mechanism of in-situ gas liberation during CO<sub>2</sub> injection in shale and tight oil reservoirs was studied. It was highlighted that, one-way CO<sub>2</sub> diffusion into live oils would trigger liberation of light hydrocarbon components. This pore-scale phenomenon would have unique characteristics that can lead to significant potentials for enhanced oil recovery and CO<sub>2</sub> storage in shale and tight formations; these effects are: (i) significant in-situ expansion of hydrocarbon phase, (ii) high immobile gas saturation due to in-situ creation of gas, and (iii) it starts with methane liberation but it grows substantially with continuous transfer of CO<sub>2</sub> into the liberated gas phase. This plausible mechanism has been largely overlooked in the reports published on EOR in shale oil reservoirs. To demonstrate the importance of this mechanism, a series of modelling analyses was performed, which required the improved EOS parameters to be able to capture the liberation of light hydrocarbon components.

The simulation results in the laboratory scales have indicated that CO<sub>2</sub> transport under diffusive-only process would lead to liberation of light hydrocarbon components in grid cells away from the fracture. This liberation of gaseous phase can increase the grid pressure by almost 100 psi, which would boost up energy of the matrix. Also, it was observed that the average oil saturation of the core (as simulated) could be reduced by 25% due to replacement with the liberated gas. Therefore, significant degree of additional oil recovery could be obtained. The liberated gas has a high CO<sub>2</sub> composition (i.e. 63%), which makes it favourable for CO<sub>2</sub> storage capacity.

In the field-scale simulations, it was identified that 9.3% of additional oil recovery would be achieved by CO<sub>2</sub> huff-n-puff. If the new mechanism was ignored, the oil recovery was halved. High gas saturation was distributed around the wellbore indicating the significant role of liberated gas on the performance of CO<sub>2</sub> EOR. Also, the CO<sub>2</sub> storage capacity of the shale reservoir would be increased markedly. Occurrence of this mechanism could reduce the soaking time significantly due to improved diffusion of CO<sub>2</sub> through the liberated gas phase. For practical implementation of CO<sub>2</sub> EOR, the impact of CO<sub>2</sub> stream impurity was analysed and, the results demonstrated that even 10% impurity would not undermine the efficiency of CO<sub>2</sub> EOR in the field-scale model. In summary, the results of this study highlights the fact that, conventional approaches for CO<sub>2</sub> EOR may be misleading for shale and tight oil reservoirs and hence, a new paradigm for evaluation of CO<sub>2</sub> EOR in shale oil reservoir is required.

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