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Influencing The CO2-Oil Interaction For Improved Miscibility And Enhanced Recovery In CCUS Projects

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Summary

In this work the physics of a fluid CO2 – crude oil mixture are explained and correlated to the evaluation of the best performance of a CO2 EOR project. The impact of different factors on the miscibility of the two fluids is described. Based on this knowledge some methods for the determination of the minimum miscibility pressure (MMP) are introduced and their pros and cons are discussed. Additionally, the concept of using miscibility enhancing additives to improve the oil recovery for successful CCUS projects is introduced. At the end a good understanding of the complex CO2 – oil mixture and its influencing parameters is developed. The reasons for good or poor miscibility are understood. An approach to make reservoirs applicable for CO2 EOR which were naturally not is shown by the application of the miscibility enhancing additives in order to improve the economics and to provide a proper justification for CCUS.

Introduction

It is obvious that storing carbon dioxide (CO_2) in geological formations provides a great opportunity to keep the greenhouse gas out of the atmosphere. Mature oil reservoirs are an optimum environment for its deposition. To add economic value and compensate for the costs connected with collecting, transport, and injecting the CO_2 it suggests itself to first use the gas beneficially.[1,2,3] CO_2 injection is established as an efficient recovery technology to collect the residual crude oil from mature fields and is applied since decades.[4] Thus, a lot of experience was gained over the last decades and the process is well understood.
However, extensive studies are necessary prior to the implementation of CO_2 EOR. This paper provides insight in its main physical principles and how the processes is influenced by adjusting the driving parameters (e.g. pressure, composition, additives …). At the end a cost and time efficient easy-to-use screening tool is described.

Physical Correlations: Understanding the Phase Behavior

One of the most determining factors for a successful and economic CO_2 EOR flood is the miscibility of the carbon dioxide and the oil in place. Under most reservoir conditions the carbon dioxide consists in its supercritical state of phase, which is a fluid that can act as a solvent. Understanding the physics behind the interaction of crude oil and carbon dioxide helps to identify the most successful procedure with the highest recovery rates. The phase behavior of crude oil (described as a blend of its heavier components C7+ and its lighter ones C1-6) and carbon dioxide reveals an extended miscibility gap as can be seen in the Gibbs triangles (cp. Figure 1, left).

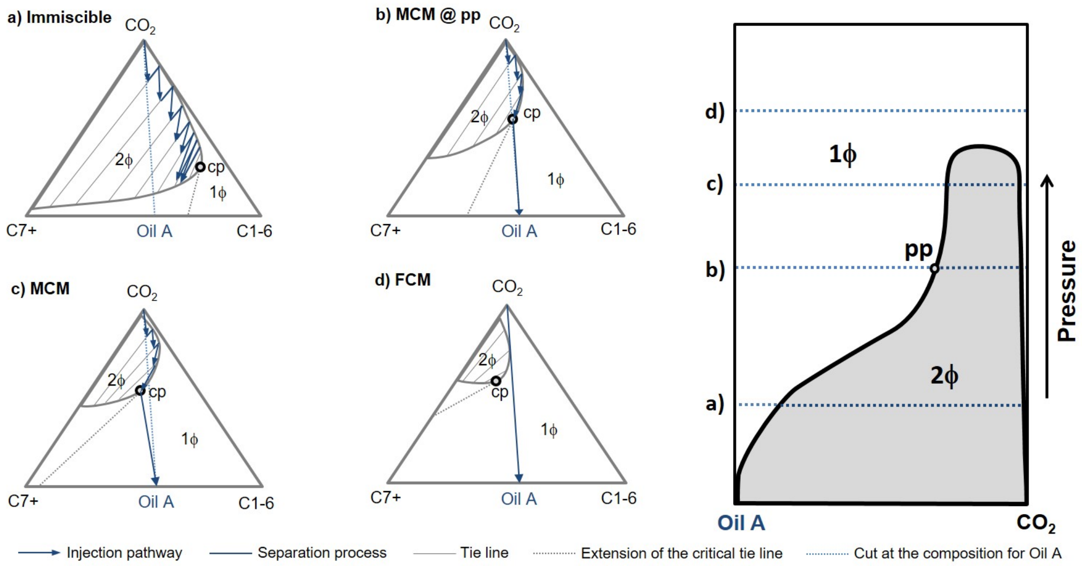

Figure 1 *Left: Gibbs triangles of the oil – CO_2 system. The miscibility gap shrinks with increasing pressure. a) The pathway crosses the miscibility gap but cannot reach the critical point. The process remains immiscible. b) The pathway crosses the critical point. Full miscibility can definitely be achieved. The corresponding pressure is the highest the MMP can have. c) Separation happens when the pathway crosses the miscibility gap but after several contacts full miscibility is achieved. (MCM) d) The composition pathway for oil A bypasses the miscibility gap and the system is fully miscible at any ratio (FCM). Right: Pseudo-binary miscibility gap for the generic oil A constructed from the Gibbs triangles a)-d). At pressure c) the cp from the triangle translates into the plait point (pp).*

The miscibility is improved with increasing pressure illustrated by the shrinkage of the miscibility gap (2ϕ) within the triangles. A pseudo-binary phase diagram showing the pressure dependency of a given oil – CO_2 mixture can be constructed from cuts through the triangles for a specific oil composition oil A (Figure 1, right). At the pressure at which this cut goes through the critical point (cp) of the miscibility gap the plait point (pp) of the pseudo-binary miscibility gap is located (cp Figure 1b).

When separation occurs two phases (2ϕ) comprising different amounts of CO_2 and the oil components C1-6 and C7+ develop. The lowest pressure at which the phases can develop full miscibility is the minimum miscibility pressure (MMP) which is characteristic for every oil. At lower pressures full miscibility cannot be achieved and the system remains immiscible. Thus, with the plait point a strong correlation between the MMP and the phase behavior is identified. [5] In a multiple contact miscible (MCM) process the composition of these phases becomes more and more equal until they are identical and merge into only one fully mixed phase (1ϕ). This is only the case if the critical point (cp) of the miscibility gap can be reached. [5] At this point thermodynamically equilibrated miscibility is achieved. From thermodynamic considerations it becomes clear, that the location of the plait point (pp) of the pressure dependent pseudo-binary system can be detected by observing the demixing process for compositions around pp. Dew point behavior is observed at CO_2 ratios higher than the composition at the pp while at higher crude oil ratios bubble point behavior is found. At pp critical separation occurs. Knowledge of the pp is of importance because its correlated pressure is the highest pressure the MMP can have for the specific system.

Flooding Processes

Considering what is discussed above the ability of the injection gas to interact with the crude oil determines the subterranean recovery process. History showed that full miscible floods are most efficient. [6] There are two types of miscible floods, first contact and multiple contact miscibility (FCM and MCM). The miscibility of the two fluids, crude oil and CO_2, depends on the pressure. A CO_2 flood applied at a pressure below the MMP is immiscible and will only deliver poor additional oil recovery. In this case the pathway crosses the miscibility gap but never reaches the critical point as can be seen in the Gibbs triangle (cp. Figure 1a). That means that separation occurs during the flooding and only the few parts of the oil which condense into the mobile CO_2 phase are produced. At the MMP the process becomes multiple-contact miscible (cp. Figure 1b and 1c). Separation processes still occur but the mixture will become fully miscible on its way through the formation. When the injected CO_2 comes into contact with the crude oil in the formation two things happen. A portion of the carbon dioxide condenses into the oil phase and causes its swelling (cp. Figure 2).

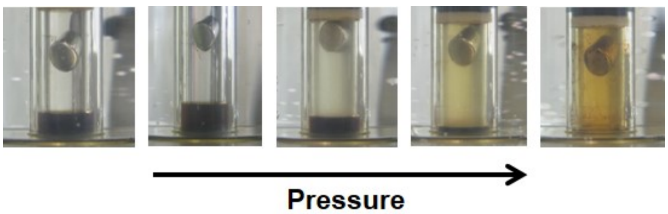

Figure 2 *Illustration of the swelling of the oil phase by CO_2 with increasing pressure.*

Due to this volume increase the crude oil is squeezed out of the pores in which it has been trapped. At the same time parts of the crude oil vaporize into the mobile CO_2 phase. With several steps of mixing and demixing these two developed phases become more and more equal in composition until the composition of the critical point is reached, where the interface disappears and only one homogeneous phase exists. At this point full miscibility is achieved. MCM floods can come with good recovery rates. Any mixture can definitely achieve full miscibility as soon as it reaches its critical point.
The process with the highest recovery efficiency is the first-contact miscibility. [6] A brief look at the phase triangles reveals, that the pathway for FCM now bypasses the miscibility gap (cp. Figure 1d). A homogeneous one-phase mixture exists at any mixing ration and no separation occurs. In most cases the pressure to achieve FCM conditions is rather high and considerably above the reservoir pressure. MCM conditions are achieved at much lower pressures and still come with high oil recovery. Thus, knowing the MMP is crucial in planning a successful CO_2 EOR flood.
In the past also so-called near miscible floods were studied. [7,8] Here a CO_2 injection slightly below the MMP was suggested. Even though the final overall oil recovery was higher than for completely immiscible condition it was not as high as a full miscible flood can achieve. In a consequence the industry interest in achieving full miscibility is high.

Lab Screening Methods

There is no standardized method for the determination of the MMP. Even though a couple of them are established and described in literature each researcher follows its own philosophy. Some work has be done to rank and compare the outcome of the different experiments. [9,10,11]
The most known experiment to determine the MMP is the slim tube method. A sand-packed tube, saturated with the oil under investigation is flooded with CO_2 at constant pressure and the recovery rate at 1.2 pore volume (PV) injected is recorded. This is repeated for a couple of pressures. From the slopes of the resulting linear plots the MMP is read. The slim tube determination is quite time consuming and expensive. For one MMP value several weeks are required and large quantities of the oil and CO_2 consumed. Furthermore, different MMPs are only comparable if the conditions are identical, e.g. the temperature, the length of the tube, or the flow rate. The lack of a standardized procedure therefore leads to incomparability of most slim tube measurements.
There are much quicker and easier to use procedures to determine the MMP. The measurement of the vanishing interfacial tension (VIFT) using the pendant drop method, for example, leads to the MMP by recording the reduction of the IFT with increasing pressure and extrapolating it to zero. It is based on the fact that the interface between the two phases, disappears for full miscibility, and obviously the IFT becomes zero. Another idea is to use the phase behavior, as described above. Detecting the miscibility of the two fluids at different ratio and pressure gives a full picture of their interaction. The phase behavior can quickly be followed visually using a pressure resistant view cell. By observing the separation process the plait point can be identified, which is correlated with full miscibility.
In opposite to the slim tube method, which is a dynamic one, the other two methods are static. In this study it is suggested to rely on phase behavior experiments, even though it is a static method while flooding a reservoir is a dynamic process. However, physics remain unchanged and the outcome is reliable. A comparison of different equilibrated systems reveals trends and shifts and is a quick and cost-saving procedure to determine the applicability of a project. Thus it is considered as a useful tool.

Miscibility Enhancing Additives

In case the reservoir pressure is lower than the MMP the reservoir will be considered not suitable for CO_2 injection in most cases. One idea is to apply miscibility enhancing additives. These chemicals are added into the CO_2 injection stream and lead to a reduction of the miscibility pressures by efficiently reducing the extent of the miscibility gaps and therewith the plait point (pp), the MMP, and the pressure required for FCM conditions are lowered (Figure 3, left). [12] Additionally, due to the improved interaction, also the swelling factor (SF) is improved (cp Figure 3, right). [13] Thus, more CO_2 condenses into the crude oil and in consequence more oil is produced due its higher mobilization.

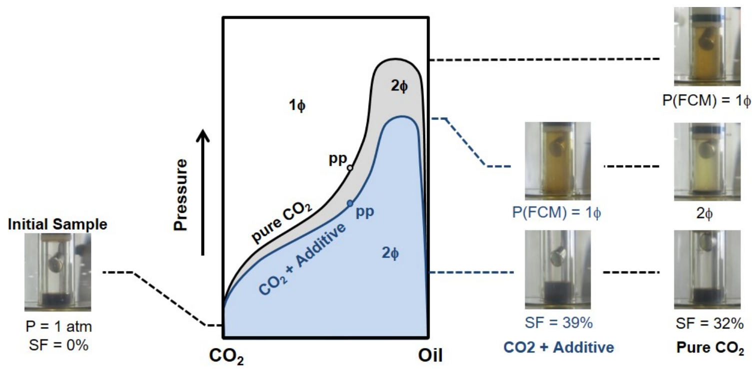

Figure 3 *With increasing pressure first the swelling factor (SF) is improved due to the additive in the CO_2 from 32% to 39%. With further increasing pressure the miscibility is continuously enhanced and thus the pressures of the plait point (pp) and for FCM conditions are lowered.*

In this way not only reservoirs are made accessible for CO_2 injection which naturally were not also the efficiency of current floods can be increased. Of course the additional cost of these additives has to be taken into account, hence the aim is to apply low dosage.

Conclusion

With good understanding of the thermodynamic relationships of fluid multi-component systems reading the phase behavior is quick but powerful experiment to evaluate the applicability of a CO_2 EOR method. Using the developed correlation between the miscibility pressure and the plait point a good estimate is possible whether a reservoir is applicable for gas injection. The performance of miscibility enhancing additives can also be screened quickly and compared reliably. The increase of the swelling factor and the reduction of the miscibility pressures are desired effects of these products which can easily be recorded and visualized. Due to their connection through the miscibility gap a shift of the plait point to lower pressure is a strong indication for a reduction of the MMP as well. Since the measurements are performed quickly a comprehensive screening of many additives can be completed in a reasonable time in order to identify the optimum balance of economics and efficiency.

The author still acknowledges that a recovery experiment like a core flood is required to estimate the overall performance of a planned flood. At the end as for each and every EOR project only a field trial can deliver the economic justification for the whole project. Nevertheless, a first step for a CO_2 EOR plan are initial lab experiments. This procedure provides a great tool for a pre-screening that does not require a great invest of time and money but allows to select the most promising technology to proceed to dynamic flooding trials.

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