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**SCALE-UP OF MISCIBLE FLOOD PROCESSES FOR
HETEROGENEOUS RESERVOIRS**

**QUARTERLY REPORT
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Introduction

The current project is a systematic research effort aimed at quantifying relationships between process mechanisms that can lead to improved recovery from gas injection processes performed in heterogeneous Class 1 and Class 2 reservoirs. It will provide a rational basis for the design of displacement processes that take advantage of crossflow due to capillary, gravity and viscous forces to offset partially the adverse effects of heterogeneity. In effect, the high permeability zones are used to deliver fluid by crossflow to zones that would otherwise be flooded only very slowly. Thus, the research effort is divided into five areas:

- Development of miscibility in multicomponent systems
- Design estimates for nearly miscible displacements
- Design of miscible floods for fractured reservoirs
- Compositional flow visualization experiments
- Simulation of near-miscible flow in heterogeneous systems

The status of the research effort in each area is reviewed briefly in the following section.

Project Status

• Development of Miscibility in Multicomponent Systems

We continue to make progress on the creation of a systematic theory of miscibility development in multicomponent systems. The mathematical theory developed at Stanford has been extended to study the effects of initial concentration of methane (CH_4) in nitrogen (N_2) floods [7]. We have demonstrated the sensitivity of the performance of high pressure displacements by N_2 or N_2 mixtures to changes in the composition of oil or the injected gas, and we have examined the development of miscibility in such systems. The analysis of four-component systems explains why the literature contains contradicting reports about the dependence of minimum miscibility pressure (MMP) on the amount of CH_4 present in the oil displaced or the injection gas. Some systems show only weak dependence on the amount of methane present, while others are quite sensitive. That behavior is explained by the positions of the tie-lines that extend through the initial and injection compositions relative to the position of the crossover tie-line. As the MMP is approached, one of those three tie-lines becomes a critical tie-line. Consider, for example, displacement of a CH_4 /butane/decane mixture by a CH_4/N_2 mixture. Whether a displacement performance is sensitive to the initial CH_4 concentration, depends on which tie-line controls development of miscibility. If the initial tie-line, which depends quite strongly on CH_4 concentration, becomes critical as the MMP is approached then the MMP is sensitive to initial CH_4 concentration. On the other hand, if the crossover tie-line controls miscibility, then the MMP is sensitive to the initial CH_4 concentration only if the crossover tie-line changes as the initial CH_4 concentration is changed. For systems with relative low initial CH_4 concentration, the crossover tie-line changes as the initial CH_4 concentration is changed. For a system with a

relatively low initial CH_4 concentration, the crossover tie-line hardly changes, so such system would be insensitive to the initial CH_4 concentration. In systems with more CH_4 present initially, however, the crossover tie-line no longer controls miscibility. Instead the initial tie-line does so, and displacement performance is again sensitive to initial CH_4 concentration. Thus very different sensitivity is observed for low CH_4 and high CH_4 concentration ranges. The analytical theory explains clearly why such behavior occurs.

A comprehensive analysis of the mass transfer involved in rising bubble experiments for determination MMP or MME has been carried out [25]. Numerical simulations of composition exchanges at the bubble interface of a three component system show that the direction that the intermediate component moves is very important for observations of the development of miscibility. When the intermediate component transfers from the liquid phase into the bubble, the composition path leads to low interfacial tension such as those that occur as in vaporizing gas drives. Whereas, in condensing gas drives, the intermediate component moves from the bubble into the surrounding liquid phase. As a result, bubble compositions near the surface moves away from critical point, and the interfacial tension increases. Thus, a single rising bubble experiment would not be able to determine MMP or MME for condensing gas drives. However, a falling drop experiment would be an alternative way to determine MME for condensing gas drives. In this version, an oil drop would descend through gas phase, and the resulting composition changes would drive the composition path close to the critical point and produce low IFT at the MME. Thus, either process mechanism could be identified by comparing rising bubble and falling drop measurements for the same compositions. Questions remain, however, concerning how to interpret bubble observations for condensing/vaporizing (C/V) displacements. Our experiments and theory indicate that it may be difficult or impossible to determine MMP or MME by the rising bubble or falling drop method for C/V displacements.

- **Design Estimates for Nearly Miscible Displacements**

In this area, we are conducting network simulations of gas injection processes with three phase flows to study the effects of interfacial tension changes on final oil recoveries. Recent experimental and theoretical results suggest that the stability of an oil layer is crucial in determining the final oil recovery of a gas injection process when all three phases move [10]. The conditions for the stability of an oil layer have been derived by examining the configurations of three phases in a single pore. The ratios of the oil/water and gas/oil interfacial tensions and capillary pressures control the stability of the oil layer. The final oil recovery are strong function of the displacement history. Detailed results from this study are presented in the results section.

- **Design of Miscible Floods for Fractured Reservoirs**

We have continued our effort of conducting experiments to quantify our three-phase gravity drainage theory developed from a vertical equilibrium analysis [5]. The theory suggests that one can obtain near-zero residual oil saturation in the upper part of a reservoir, if the reservoir is water-wet, and the system has a positive initial spreading coefficient. Experiments have been carried out on water-wet sand columns using systems of water, hydrocarbons and air. Hexane (C_6), iso-octane (iC_8) and decane (C_{10}) have been used to vary the oil phase properties. Measurements for hexane systems show that the residual oil saturations in the

upper part of the column can be as low as 0.1 % of the pore volume. However, for decane systems, which has a negative initial spreading coefficient, the residual oil saturations in the upper part are about 2.0 % of pore volume. Investigations on the effects of wettability on residual oil saturations are also in progress.

Our high pressure drainage experiment continues producing new data from drainages of Means crude in the presence of CO₂. We have obtained results from drainage of Means at pressures of 900, 1500, and 1700 psia on two sandstone cores of 100 and 500 mD. Our data have shown that increases in pressure (for the same temperature) result in increases in oil recovery, as a result, we believe, of the reduction in interfacial tension between gas and oil phases.

- **Flow Visualization Experiments**

We have extended our effort on conducting visualization experiments. We have performed two-phase displacements of matched viscosity but different densities to investigate gravity effects without the influence of stabilizing or unstabilizing created by viscous forces. The observations from those experiments will be reproduced by the particle-tracking simulator. Undergraduate student Bradley Peters is conducting experiments to investigate the scaling parameters for gravity and viscous forces in layered systems, by comparing the fluid distributions on two models of same heights but different lengths.

- **Simulation of Flow in Heterogeneous Reservoirs**

We have continued to investigate the streamline approach as a numerical alternative to conventional finite difference simulators to be used in predicting near-miscible gas injection in heterogeneous reservoirs. The streamline method has been generalized to include gravity, compositional effects and dispersion in three dimensions [3]. In cases where the principal flow directions are governed by the pattern of permeability, comparisons of results from high resolution simulation and streamline techniques show that streamline techniques can predict flow patterns accurately and are free from numerical dispersion in two to four orders of magnitude less computer time.

A new effort in this area has been started and has made substantial progress. Darryl Fenwick is building a three-dimensional network model for three-phase flows. This network model is aimed to generate three-phase relative permeabilities by taking into account detailed mechanisms of three-phase flow in the pore levels. This model will also be able to evaluate the relative contributions of various flow mechanisms to macroscopic flow behaviors in different systems.

Research Results

In this section, we report in some detail our results from pore-level modelling of three-phase flow in porous media. The research results reported have been obtained by PhD student Darryl Fenwick working with Prof. Martin Blunt.

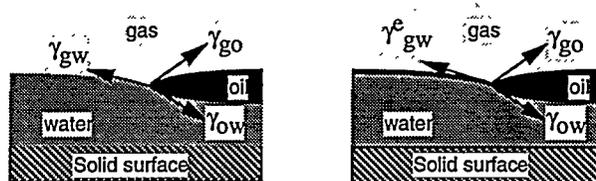


Figure 1: Three fluids in contact near a solid surface.

Introduction

Three-phase flow is an important process in enhanced oil recovery, gravity drainage, solution gas drives and in pollutant transport and clean-up. Multiphase flow in porous media is characterized by capillary pressure and relative permeability functions. For three-phase flow, they are extremely difficult to determine for the full range of saturation values. For a recent study see Kalaydjian et al.[15]. Simulation studies rely on empirical correlations to compute relative permeability. These are either fits to the experimental data or correlations that extrapolate the two-phase (gas/water, oil/water and gas/oil) functions into the three-phase region [2, 9, 23]. These functions cannot properly represent the intricacies of the flow phenomena. To understand three-phase flow in porous media, we need to study the physics at the pore level. When three phases are in contact with other, their behavior is partly determined by the spreading coefficient C_s , which is defined as:

$$C_s = \gamma_{gw} - (\gamma_{ow} + \gamma_{go}) \quad (1)$$

where initially γ_{gw} , γ_{ow} and γ_{go} are the gas/water, oil/water and gas/oil interfacial tensions respectively, measured on pure fluids before they are brought into contact with each other. Three different situations can arise [13]. (i) If $C_s < 0$, the three-phase contact line shown in Figure 1 is stable. Examples include medium and long chain alkanes, such as dodecane in contact with air and water. (ii) If $C_s > 0$, the contact line between the three phases is unstable and the oil spreads. Many solvents, hydrocarbons and crude oils (see p. 104, Table 5 of Muskat[18]) have a positive spreading coefficient. We can define an equilibrium spreading coefficient C_s^e from Equation (1), where the interfacial tensions are measured in thermodynamic equilibrium. If $C_s > 0$, the water surface is coated by a thin oil film, which lowers the effective gas/water interfacial tension and $C_s^e < 0$. Excess oil remains in a droplet in equilibrium with the film. Many hydrocarbons, such as benzene, and solvents, such as carbon tetrachloride, have a positive initial spreading coefficient, but a negative equilibrium spreading coefficient. The film generally is approximately of molecular thickness, between 0.5 and 5 nm across. (iii) The third possibility is that the oil film can swell without limit. Once the oil film is thicker than the range of intermolecular forces, $C_s^e = 0$ [1, 11, 21]. An example of this behavior is Soltrol 170, a commercial mixture of hydrocarbons [19, 24]. In the rest of this report, we will assume that the system has reached thermodynamic equilibrium, and hence the distribution of fluid is controlled by the equilibrium spreading coefficient, which is either zero or negative.

If gas is introduced into a system containing water and residual oil, spreading allows the oil to form a continuous layer between gas and water, enabling the oil to flow. This phenomenon has been suspected as an important mechanism for oil recovery by inert gas injection since the work of Dumore and Schols [8] and was confirmed by careful experimental measurements on

sandstone cores and unconsolidated media [4, 6, 16, 24]. The drainage of oil layers has been directly observed using two-dimensional etched glass micromodels by Kantzas et al. [17], Oren et al. [19] and Kalaydjian [14]. Kalaydjian and Oren et al. demonstrated that a system with a positive value of C_s gives better oil recovery than one where $C_s < 0$. Recently, three-phase gravity drainage has been studied theoretically and experimentally. It has been shown that flow in stable oil layers in crevices of the pore space enable very low residual oil saturations to be achieved [5].

Three-phase flow allows a series of double displacement mechanisms, where one fluid displaces another that displaces the third. This was observed and described by Oren et al. [19] with reference to double drainage, where gas displaces oil that displaces water. Here we will describe a three-phase pore level numerical model that incorporates the effects of oil layers and double displacement mechanisms. A percolation network model of three-phase flow was first proposed by Heiba et al. [12], and more sophisticated models including the effects of flow in oil films [22] and both oil films and double drainage [20] have been shown to reproduce the results of two-dimensional micromodel experiments. This model will extend the previous work to three dimensions and to include the full range of possible drainage and imbibition mechanisms. We demonstrate how our description of the pore level physics inevitably leads to a macroscopic description of three-phase flow that is very different from the conventional Darcy law formulation.

A Pore Level Network Model

We represent the pore space as a cubic array of wide pores connected together by narrower throats. Arbitrary distributions of pore and throat radii may be specified, except that a pore is always larger than any of the six throats connected to it. In this model both the pores and throats have a square cross-section, although this restriction can be changed easily. The flow of three phases is simulated by allowing a sequence of individual pore events [10]. Oil flow through a stable oil layer has been found to be one of the controlling mechanisms in determining final oil saturation [10]. The stability analysis of an oil layer in the pore space is discussed below.

An Oil Layer in the Pore Space

Figure 2 shows three phases in a wedge. We will assume that the water is wetting and that the oil/water contact angle is smaller than the gas/oil contact angle. This arrangement may be stable even if the spreading coefficient is negative. The oil layer here will be of order a few microns thick—much thicker than the nanometer-sized molecular oil films seen on flat surfaces. The radius of curvature of the gas/oil interface is r_{go} , and the curvature of the oil/water interface is r_{ow} . We assume that there is no curvature in the direction perpendicular to the plane of Figure 2. Then from the Young-Laplace equation $P_{cgo} = \gamma_{go}/r_{go}$, where P_{cgo} is the local gas/oil capillary pressure, with a similar expression for P_{cow} , the oil/water capillary pressure. We define:

$$R = \frac{r_{go}}{r_{ow}} = \frac{\gamma_{go}P_{cow}}{\gamma_{ow}P_{cgo}}. \quad (2)$$

For large values of R , the oil layer is thick. At a critical value, R_c , the arrangement of fluid shown in Figure 2(a) is no longer possible, and it is unlikely that the oil layer remains stable. This happens when the point of contact of the oil/water interface with the surface and the gas/oil

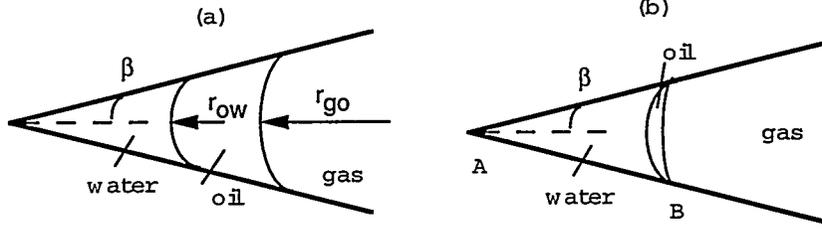


Figure 2: (a). Three phases in a wedge of half angle β . (b) At this point, the oil layer first becomes unstable.

contact coincide, as shown in Figure 2(b). The distance AB marked on Figure 2(b) is:

$$AB = r \frac{\cos(\theta + \beta)}{\cos\beta}, \quad (3)$$

for an interface of radius r , contact angle θ and wedge of half angle β . Hence the critical ratio R_c is:

$$R_c = \frac{\cos(\theta_{ow} + \beta)}{\cos(\theta_{go} + \beta)}. \quad (4)$$

If we consider the case where the water is completely wetting and covers the solid surface with a thin film of molecular thickness, then the microscopic arrangement of water, gas and oil at the solid surface is similar to that illustrated in Figure 1, except that the water surface is flat. The vertical force balance is maintained by intermolecular forces in the water film, but the horizontal balance of forces implies that

$$\gamma_{gw} = \gamma_{go} \cos\theta_{go} + \gamma_{ow}, \quad (5)$$

or:

$$\cos\theta_{go} = 1 + \frac{C_s^e}{\gamma_{go}}, \quad (6)$$

as derived by Kalaydjian [14, 15]. Notice here we have used the equilibrium value of the spreading coefficient because the water film may itself be coated by a thin film of oil.

If we use Eq. (6) for the gas/oil contact angle and assume that $\theta_{ow} = 0$, then, after some algebra, Equation (4) becomes:

$$\frac{1}{R_c} = 1 + \frac{C_s^e}{\gamma_{go}} - \left(-\frac{C_s^e}{\gamma_{go}} \right)^{\frac{1}{2}} \left(2 + \frac{C_s^e}{\gamma_{go}} \right)^{\frac{1}{2}} \tan\beta. \quad (7)$$

As an example, consider benzene in contact with water and air, for which $C_s^e = -1.6mNm^{-1}$ and $\gamma_{go} = 28.8mNm^{-1}$. Then for a square wedge with $\beta = \pi/4$, $R_c = 1.6$. An oil layer is stable for larger values of R and is unstable for R below this critical value. If the equilibrium spreading coefficient is zero, $R_c = 1$.

This is a very simple geometric argument for the stability of an oil layer in a wedge that ignores the complex geometry of a real pore space. However, the analysis does give an indication of the expected behavior: oil layers are stable even for negative spreading coefficient, but that

the range of capillary pressures over which a layer is stable decreases with decreasing spreading coefficient.

When oil layers are stable, the oil is connected and cannot be trapped in the presence of gas. This allows very low oil saturations to be achieved during gas injection. For $R < R_c$ there are no oil layers and oil can be trapped by both gas and water. If the initial spreading coefficient is positive, the water will still be coated by an oil film of molecular thickness, but this film is far too thin to allow any significant oil flow. The flow of oil through molecular films will be ignored in the calculations that follow.

How the Network Model Simulates Fluid Invasion

Displacement proceeds by one pore or throat filling at a time. The capillary pressures for all the possible displacement processes mentioned in the previous section are stored in a sorted list. At the beginning, the model is completely saturated with water. Fluid is injected through one face of the model and produced through the opposite face. There are periodic boundary conditions in the other two directions. Oil is injected into the network. Subsequently, water, gas or oil may all be injected and displaced in any order. When all three phases are present in the model, two capillary pressures must be specified. If we specify P_{cgo} and P_{cow} , the gas/water capillary pressure is defined as $P_{cgw} = P_{cgo} + P_{cow}$. We hold one of the capillary pressures constant, say the gas/oil pressure. We then make a small change in the oil/water capillary pressure. Let us assume that we are considering drainage, which means that the oil/water capillary pressure is increasing. We then find, of all possible two-phase and three-phase displacements, the one that has the lowest oil/water capillary pressure assuming that P_{cgo} is some known, fixed value. This could be an event where oil displaces water, oil displaces gas, or gas displaces water, or one of the double displacement mechanisms. For imbibition, we would find the event with the highest oil/water capillary pressure. In the next step we may either keep P_{cgo} constant and proceed as before, or hold P_{cow} fixed at its previous value. In the latter case we perform the displacement with the lowest value of P_{cgo} (for a drainage step) or the highest value (for imbibition).

If a phase, for instance oil, does not span the network, we can still define local oil/water and gas/oil capillary pressures. These are found from the radii of curvature of the last pore or throat that oil either invaded or was displaced from. The network model simulates any sequence of three phase flow by incremental changes in capillary pressure. The saturations of each phase at each step are recorded. As an example, Figure 3 is a picture of a two-dimensional three phase simulation on an 80 by 80 network. The picture shows gas breakthrough during gas injection into water and oil.

Why a Conventional Darcy Law Description Cannot be Valid

Figure 4 shows the saturation path and corresponding capillary pressures for three-phase displacements with a zero spreading coefficient simulated on a 20 by 15 by 15 network. Initially the network model is completely saturated with water. The oil/water capillary pressure is then increased to 11,000 Pa, where the water saturation is 15%. Waterflooding was then simulated, and the resulting residual oil saturation in water was just over 30%. We model the injection of gas for two cases. The first, indicated by the solid line, is when the oil/water capillary pressure is increased to and then maintained at 11,000 Pa. This represents the injection of gas into connate water and oil. All the oil is recovered. Before the gas is injected, all the oil is connected. The

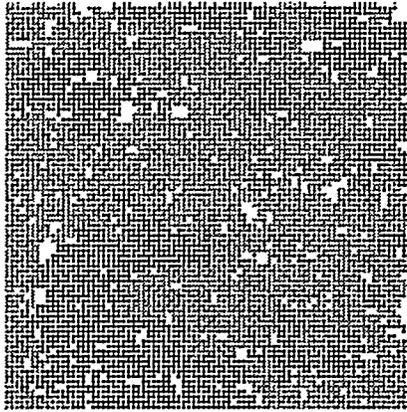


Figure 3: Gas injection into oil and water at gas breakthrough simulated on an 80 by 80 square network. The fluids have a spreading coefficient of zero. Gas is gray, oil is black and water is white. Both the water and oil phases are connected through layers in the corners of the pore spaces.

oil/water capillary pressure is determined by the smallest throat that the oil has entered. When the gas is first injected, oil layers are stable and so the oil remains connected. For zero spreading coefficient, the point at which oil layers disappear, when $R = R_c = 1$ in Figure 4, also corresponds exactly to the gas/oil capillary pressure necessary for gas to enter the smallest oil filled throat. Thus the gas is able to displace all the oil while oil layers are present, resulting in 100% recovery. This is the ideal case.

The dotted line in Figure 4 indicates gas injection into waterflood residual oil and water. In this simulation the oil phase never spans the network. Oil layers are no longer stable at a lower value of P_{cgo} than in the first example. Not all the oil has been contacted by gas when the layers disappear. The remaining oil recovery for $R < R_c$ is the result of double drainage alone. The final oil saturation, when $P_{cgo} = 42,000 Pa$ (off the scale in Figure 4) is 20%, approximately 10% lower than the waterflood residual.

Figure 5 illustrates the same two displacements for fluids with an equilibrium spreading coefficient of $-4mNm^{-1}$, similar to a decane/water/air system [13]. In this example, oil layers are stable for a more restricted range of capillary pressure, as indicated in the Figure 5. For both cases, drainage through stable oil layers makes very little contribution to recovery, and displacement of oil is predominantly by double drainage. Notice that for gas injection into waterflood residual oil, the final oil saturation is virtually the same as for the zero spreading coefficient case. In contrast, injection into a higher oil saturation now recovers much less oil and the remaining oil saturation (40%) is higher than the waterflood residual (35%).

The conventional multiphase Darcy law relates the oil flow to a pressure gradient in the oil phase. If the oil is not connected, but there is recovery by double drainage, we have oil flow with no macroscopic pressure gradient in the oil. This process can only be modeled by cross-terms, where the flow of oil is related to pressure gradients in the continuous gas and water phases. This demonstrates one inadequacy of conventional three-phase relative permeability models.

Hysteresis, where we get different final oil saturations after gas injection, depending on the saturation (or capillary pressure) history, is also seen in two-phase flow, but in three-phase flow, particularly at low oil saturation, we have shown that it is very significant.

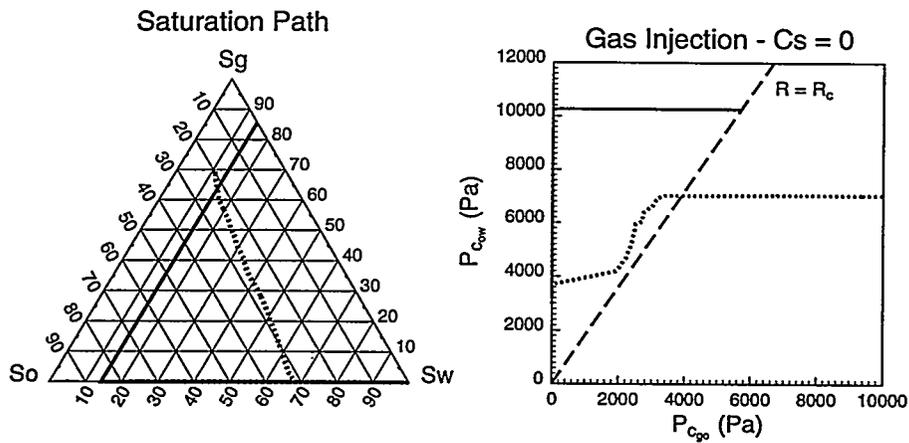


Figure 4: Different pathways in capillary pressure and saturation space, representing gas injection into waterflood residual oil for fluids with a spreading coefficient of zero.

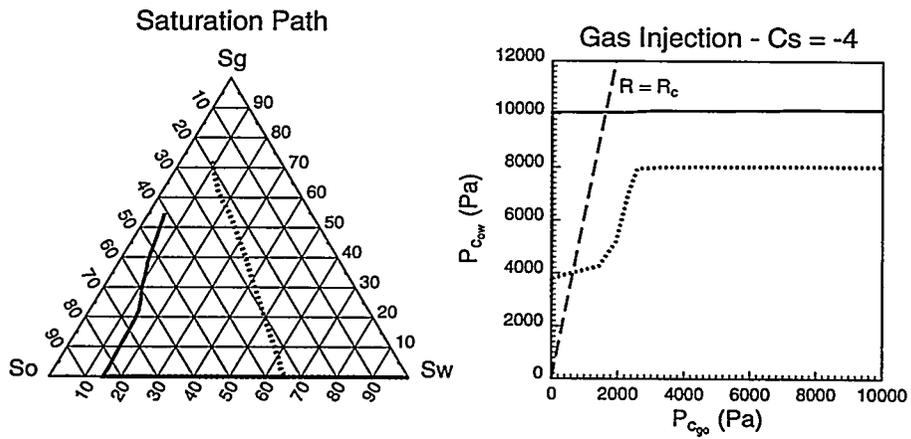


Figure 5: Different pathways in capillary pressure and saturation space, representing gas injection into waterflood residual oil for fluids with a spreading coefficient of $-4mNm^{-1}$.

How could we use the network model to predict the oil recovery from gas injection? We have demonstrated that the residual oil saturation is sensitive to capillary pressure history, but we have no way of knowing *a priori* what route in capillary pressure space a given displacement would take. Imagine that we attempt to predict a one-dimensional displacement where gas is injected into waterflood residual oil. Conventionally we would use predetermined relative permeability and capillary pressure functions in the conservation equations for the fluid phases. We could solve the equations and find the route in capillary pressure space that the displacement takes at some fixed spatial location. However, we have just shown that the final oil saturation and consequently the relative permeability and capillary pressure is a strong function of this path. For instance, if an oil bank of large oil saturation develops we would predict very good recovery for zero spreading coefficient, whereas if no oil bank is formed this corresponds to gas injection with a low value of P_{cow} and the recovery is much poorer. Using a network model we can compute capillary pressure and relative permeabilities for a given pathway in capillary pressure space. A discussion of this will be the topic of later work. We must find relative permeabilities and capillary pressures which when placed in a conservation equation give the same sequence of saturation changes that were used to compute them in the first place. This self-consistency requirement is particularly important for a correct understanding of the mobilization of residual oil by gas and water. This can be achieved using network modeling, but clearly cannot be incorporated in conventional numerical models, nor readily measured experimentally for the full range of possible types of displacement.

Conclusions

In thermodynamic equilibrium, the spreading coefficient of oil between water and gas is either zero, or negative. However, it is still possible for three bulk phases to coexist in a pore throat, and we found the conditions in which a oil layer would be stable in a wedge.

We have described a three-dimensional, three phase network model that incorporates three-phase drainage and imbibition displacement mechanisms. We have demonstrated that conventional models of capillary pressure and relative permeability are likely to give an inadequate representation of oil flow at low saturation, because of the significant and subtle effects of hysteresis. We showed this by considering different possible sequences of saturation changes during gasflooding. Further work on a description of three-phase flow in a variety of different circumstances is planned.

References

- [1] Adamson, A. A.: *Physical Chemistry of Surfaces*, John Wiley & Sons, Inc., New York (1990).
- [2] Baker, L. E.: "Three-Phase relative Permeability Correlations," paper SPE 17369 presented at the 1988 Sixth Symposium on Enhanced Oil Recovery, Tulsa, OK, April.
- [3] Blunt, M. J. Liu, K. and Thiele, M. R.: "A Generalized Streamline Method to Predict Reservoir Flow," (May 1991) 8th European Symposium on Improved Oil Recovery, Austria.
- [4] Blunt, M.J., Fenwick, D. and Zhou, D.: "What Determines Residual Oil Saturation in Three Phase Flow?," paper SPE 27816 presented at the 1994 Ninth Symposium on Improved Oil Recovery, Tulsa, OK, April.

- [5] Blunt, M.J., Zhou, D., and Fenwick, D.H.: "Three Phase Flow and Gravity Drainage in Porous Media," in press, *Transport in Porous Media* (1995).
- [6] Chatzis, I., Kantzas, A. and Dullien, F. A. L.: "On the Investigation of Gravity-Assisted Inert Gas Injection Using Micromodels, Long Berea Sandstone Cores, and Computer-Assisted Tomography," paper SPE 18284 presented at the 1988 SPE Annual Technical Conference and Exhibition, Houston, TX, October 2-5.
- [7] Dindoruk, B., Orr, F. M. Jr. and Johns, R.: "Analytical Theory of Multicontact Miscible Displacement with Nitrogen," (October 1995) manuscript in preparation, paper SPE 30771 to be presented at the 1995 SPE Annual Technical Conference and Exhibition, Houston, TX.
- [8] Dumoré, J.M. and Schols, R.S.: "Drainage Capillary Pressure Functions and the Influence of Connate Water," *Soc. Pet. Eng. J.* (1974) 437-444.
- [9] Fayers, F. J.: "Extension of Stone's Method 1 and conditions for real characteristics in three-phase flow," *SPE Reservoir Engineering* (1989) 4, 437-445.
- [10] Fenwick, D. H. and Blunt, M. J.: "Pore Level Modelling of Three-Phase Flow in Porous Media," (May 1991) 8th European Symposium on Improved Oil Recovery, Austria.
- [11] Gibbs, J. W.: *The Collected Works of J. Willard Gibbs*, Longmans, Green, New York (1928).
- [12] Heiba, A. A., Davies, H. T. and Scriven, L. E.: "Statistical Network Theory of Three-Phase Relative Permeability," paper SPE 12690 presented at the 1984 Fifth Symposium on Enhanced Oil Recovery, Tulsa, OK, April.
- [13] Hirasaki, G.J.: "Structural interactions in the wetting and spreading of van der Waals fluids," *J. Adhesion Sci. Technol.* (1993) 7, No. 3, 285-322.
- [14] Kalaydjian, F. J.-M.: "Performance and Analysis of Three-Phase Capillary Pressure Curves for Drainage and Imbibition in Porous Media," paper SPE 24878 presented at the 1992 SPE Technical Conference and Exhibition, Washington, D.C.
- [15] Kalaydjian, F. J.-M., Moulu, J.-C., Vizika, O. and Munkerud, P. K.: "Three-Phase Flow in Water-Wet Porous Media: Determination of Gas/Oil Relative Permeabilities under Various Spreading Conditions," paper SPE 26671 presented at the 1993 SPE Technical Conference and Exhibition, Houston, TX.
- [16] Kantzas, A., Chatzis, I. and Dullien, F. A. L.: "Enhanced Oil Recovery by Inert Gas Injection," paper SPE 17379 presented at the 1988 Sixth Symposium on Enhanced Oil Recovery, Tulsa, OK, April.
- [17] Kantzas, A., Chatzis, I. and Dullien, F. A. L.: "Mechanisms of Capillary Displacement of Residual Oil by Gravity-Assisted Inert Gas Injection," paper SPE 17506 presented at the 1988 Rocky Mountain Regional Meeting, Casper, WY.
- [18] Muskat, M.: *Principles of Oil Production*, McGraw Hill, Boston (1949).
- [19] Oren, P. E., Billiotte, J. and Pinczewski, W. V.: "Mobilization of Waterflood Residual Oil by Gas Injection for Water-Wet Conditions," *SPE Formation Evaluation* (March 1992) 70-78.

- [20] Ören, P-E., Billiote, J., and Pinczewski, W.V.: "Pore-Scale Network Modelling of Waterflood Residual Oil Recovery by Immiscible Gas Flooding," paper SPE 27814 presented at the 1994 1994 Improved Oil Recovery Symposium, Tulsa, OK, April.
- [21] Rowlinson, J. S.: *Molecular Theory of Capillarity*, Clarendon Press, Oxford (1989).
- [22] Soll, W. E., Celia, M. A.: "A Modified Percolation Approach to Simulating Three-Fluid Capillary Pressure-Saturation Relationships," *Advanced in Water Resources* (1993) 16, 107-126.
- [23] Stone, H. L.: "Estimation of three-phase relative permeability and residual data," *Journal of Canadian Petroleum Technology* (1973) 12, 53-61.
- [24] Vizika, O.: "Effect of the Spreading Coefficient on the Efficiency of Oil Recovery with Gravity Drainage," Presented at the Symposium on Enhanced Oil Recovery, presented before the Division of Petroleum Chemistry, Inc., Denver, Colorado (1993).
- [25] Zhou, D. and Orr, F. M. Jr.: "An Analysis of Rising Bubble Experiments for Determination of Minimum Miscibility Pressure (MMP)," (October 1995) manuscript in preparation, paper SPE 30786 to be presented at the 1995 SPE Annual Technical Conference and Exhibition, Houston, TX.