Interfacial Effects in the Recovery of
Residual Oil by Displacement: Work at

Northwestern University

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INTERFACIAL EFFECTS IN THE RECOVERY
OF RESIDUAL OIL BY DISPLACEMENT:
STUDIES AT NORTHWESTERN UNIVERSITY

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Objective A: Further Analysis of the Displacement of Oil by Water in Porous Media (S. G. Oh and J. C. Slattery)

Abstract

In order to investigate the effects of interfacial tension and of wettability upon the tertiary recovery of residual oil by a low interfacial tension waterflood, we have carried out a static analysis of a single irregular pore partially filled with residual oil. There is a critical value for the pressure drop over this pore below which the residual oil can not be displaced but instead will assume a static configuration.

In carrying out this computation, we have idealized the pore by saying that its radius is a sinusoidal function of axial position. We have recognized that the pressure drop across the pore under static conditions is a function of the pore geometry, the volume of the oil segment, the position of the oil segment in the pore, the crude oil-water interfacial tension, the advancing contact angle, and the receding contact angle. We have taken the relationship between the advancing and receding contact angles to be the class III behavior established by Morrow (1974) for roughened polytetrafluorethylene surfaces.

As the result of this analysis, we find that, for the most efficient displacement of residual oil, the porous structure should be water-wet. Intermediate wettability may be less desirable than either oil-wet or water-wet behavior.

The discussion of displacement in a single pore is extended in the form of an estimate for the critical value of $\frac{|\nabla P| k}{\gamma}$ required for significant recovery of residual oil from sandstones. A comparison is offered with data taken from the literature.

Introduction

Petroleum is found in the microscopic pores of sedimentary rocks such as sandstones and limestones. Not all of the pores will be filled with petroleum. Some of the pores will contain water or brine that is saturated with the minerals in the local rock structure.

In the primary stage of production, oil and brine are driven into a well from the surrounding rock by the relatively large difference between the initial field pressure and the pressure in the well. Perhaps 10-20% of the oil originally in place is recovered in this manner (Geffen 1973).

In the secondary stage of production, water or steam is pumped into a selected pattern of wells in a field forcing a portion of the oil into other production wells. The void volume in a permeable rock may be thought of as many intersecting pores of varying diameters. Consider a particular pore that bifurcates to form two pores of unequal diameters, which in turn rejoin at some point downstream. A segment of oil (residual oil) will be trapped in that pore through which the oil is displaced by the water more slowly. In this manner, 10-40% of the oil initially in place will be recovered (Geffen 1973), but 50-70% of the oil originally in place is left behind in the field.

A number of tertiary recovery techniques have been proposed (Geffen 1973). We will focus our attention here on the recovery of residual oil by a low interfacial tension waterflood in which the crude oil is relatively insoluble.^a It has been estimated that in carefully selected, well-designed,

a One can distinguish between at least two different types of surfactant waterfloods.

In the type with which we are concerned here, a large volume, 15 to 60%

good performing operations an additional 30% of the oil originally in place might be recovered by a low interfacial tension waterflood (Geffen 1973).

The crude oil-water interfacial tension can be reduced orders of magnitude by adding to the waterflood either a mixture of surfactants or an alkaline solution.

Foster (1973), Gale and Sandvik (1973), Hill et al. (1973), and Cash et al. (1975) have reported significant recovery of residual oil in laboratory tests using waterfloods to which small amounts of petroleum sulfonate had been added. Depending upon the particular petroleum sulfonate used and upon the salt concentration, crude oil-water interfacial tensions as low as 10^{-2} to 10^{-4} dyne/cm were obtained.

(a continued from previous page)

of the pore volume or more (Gogarty 1976), of a dilute surfactant solution is used. The crude oil is nearly insoluble in the surfactant solution and we speak of an immiscible displacement.

In the second type, a smaller volume, 3 to 20% of the pore volume (Gogarty 1976), of a more concentrated surfactant solution is used. The concentration of the surfactant solution is sufficiently high to ensure that the crude oil is miscible with the crude oil in all proportions. As a small slug of this surfactant solution moves through the porous structure mixing with and displacing the crude oil, surfactant is lost by adsorption on the rock and the solution is further diluted with the connate water present in the structure. As the concentration of surfactant falls, the water-crude oil-surfactant mixture can move from the single phase region to the multipase region on its phase diagram. We should expect that a miscible displacement carried out with a small slug of surfactant solution will revert to an immiscible displacement at some point in the reservoir.

For a further discussion of these points, see Healy and Reed (1974), Healy et al. (1975), Gilliland and Conely (1975), and Gogarty (1976).

Some crude oils contain organic acids that can react with an alkaline waterflood to produce a mixture of surfactants at the crude oil-water interface. These surfactants reduce the crude oil-water interfacial tension. Both Jennings et al. (1974) and Cooke et al. (1974) have reported significant recovery of residual oil in laboratory tests using low-interfacial-tension, alkaline waterfloods. Earlier studies of alkaline waterflooding by Leach et al. (1962), by Mungan (1966), and by Emery et al. (1970) emphasized the effects of wettability upon the recovery of residual oil rather than the effects of interfacial tension.

Taber (1969) and Taber et al. (1973) observed from their experimental studies that in any particular displacement there is a critical value of $\frac{|\nabla P|}{\gamma}$ below which no residual oil can be obtained by waterflooding. Here γ is the crude oil-water interfacial tension and $|\nabla P|$ is the magnitude of the pressure gradient. Foster (1973) found that there was a critical value of $\frac{v_w \mu_w}{\psi \gamma}$ below which no residual oil could be recovered by waterflooding and that there was a minimum value of $\frac{v_w \mu_w}{\psi \gamma}$ required for complete recovery of the residual oil. Here v_w is the magnitude of the Darcy velocity of the aqueous phase, μ_w is the viscosity of the aqueous phase, and ψ is the porosity of the structure. These observations are confirmed by Ehrlich et al. (1974), who suggest that there is a maximum value of $\frac{|\nabla P| k}{\gamma \psi}$ below which the production of residual oil can not be initiated. By k we mean the permeability of the structure.

Purcell (1950) and Melrose (1965, 1970) used a doughnut-shaped pore model in discussing capillary pressure during imbibition and drainage. Melrose and Brandner (1974) used the results of Melrose (1965, 1970) to estimate the minimum value of $\frac{v_w \mu_w}{\psi \gamma}$ required for the complete recovery of residual oil.

Experimental evidence suggests that an oil-water interface will not advance through a pore smoothly as a function of time. Poynting and Thomson (1902) forced mercury up a capillary tube and then gradually reduced the pressure. Instead of falling, the mercury at first adjusted itself to the reduced pressure by altering the curvature of the air-mercury interface. When the pressure gradient finally grew too large, the configuration of the meniscus became unstable and the mercury fell a short distance in the tube before stopping, repeating the deformation of the interface, and falling again when a new instability developed. Consequently, they observed the interface to move through the tube in a series of jumps. Yarnold (1938) saw this same jumping phenomena as a segment of liquid moved slowly through a glass capillary tube. Heller (1968) used high-speed photography to follow the advance of water-air interfaces through a porous bed as jumps in the individual pores. He found that any 7.8×10^{-6} sec.

Using an integral momentum balance for the oil and water in an irregular pore during the period of slow deformation between jumps, Slattery (1974) constructed a qualitative theory for the entrapment of oil during a secondary waterflood and for the displacement of residual oil by a tertiary low interfacial tension waterflood. This qualitative theory led to a number of conclusions, two of which are of particular interest here.

- 1) There is a critical value for $\frac{|\nabla P| k}{\gamma}$ below which no residual oil can be recovered by displacement in either oil-wet or water-wet rock. ^b

^b Slattery's (1974) conclusions apply either to a particular pore structure or to a set of geometrically similar porous media (perhaps a family of sandstones, the different members of which are distinguished by different permeabilities). For geometrically similar porous media, porosity ψ is a constant. It is therefore equivalent to speak either of the critical value

- ii) The efficiency of residual oil recovery in both oil-wet and water-wet rock will increase as $\frac{|\nabla P| k}{\gamma}$ continues to increase above its critical value.

For experimental confirmation of these two conclusions, see Taber (1969), Taber et al. (1973), Foster (1973, and Ehrlich et al. (1974).

This problem is more amenable to quantitative analysis, if we consider a single irregular pore partially filled with residual oil. There is a critical pressure drop over this pore below which the segment of oil it contains will not be displaced. Below this critical value, as the pressure drop is increased, the segment of oil assumes a sequence of static configurations.

Our initial objective in what follows is to determine for a single irregular pore partially filled with residual oil the critical value for this pressure drop, below which the residual oil can not be displaced but instead will assume a static configuration. In carrying out this computation, we idealize this single irregular pore by saying that its radius is a sinusoidal function of axial position as shown in Figure 1. We recognize that the pressure drop across the pore under static conditions is a function of the pore geometry, the volume of the oil segment, the position of the oil segment in the pore, the crude oil-water interfacial tension, the advancing contact angle, and the receding contact angle.

b continued

of $\frac{|\nabla P| k}{\gamma}$ or the critical value of $\frac{|\nabla P| k}{\gamma}$ (Ehrlich et al. 1974), since these critical values should in general be expected to be functions of the geometry of the pore structure, the advancing contact angle, and the receding contact angle.

The results of this computation form the basis for a quantitative estimate of the critical value of $\frac{|\nabla P| k}{\gamma \psi}$ required for the significant recovery of residual oil by a low interfacial tension waterflood. We conclude by comparing our predictions with data from the literature.

Single Pore

Let us determine for a single irregular pore partially filled with residual oil the critical value for the pressure drop across the pore, below which the residual oil can not be displaced but instead will assume a static configuration. We will begin by calculating under static conditions the pressure drop as a function of the pore geometry, the volume of the oil segment, the position of the oil segment in the pore, the crude oil-water interfacial tension, the advancing contact angle, and the receding contact angle. The critical pressure drop is its maximum value as a function of the position of the oil segment in the pore.

The real physical problem is idealized by the following assumptions.

1. The pore is axially symmetric; its radius is a sinusoidal function of axial position as shown in Figure 1.
2. There is only one segment of oil in the pore.
3. Both the oil and the water are incompressible fluids. The volumes of the various phases do not change as the oil segment assumes a sequence of static configurations in the pore.
4. There is incipient motion from left to right in Figure 1; θ_1 is an advancing contact angle and θ_2 is a receding contact angle.

5. The interfacial tension, the advancing contact angle, and the receding contact angle are independent of the position of the oil segment.
6. The force of gravity can be neglected with respect to the pressure drop over the pore.

With reference to Figure 1, Laplace's equation applied to the receding (left) interface requires

$$P_{\text{upstream}}^{(w)} - P^{(o)} = -2H^{(w,o)} \gamma \quad (1)$$

where $P_{\text{upstream}}^{(w)}$ is the pressure in the water upstream of the oil segment, $P^{(o)}$ is the pressure within the oil segment, and

$$H^{(w,o)} = \frac{\cos \theta_1 - \left(\frac{A\pi}{L}\right) \sin \theta_1 \sin \left(\frac{2\pi z_1}{L}\right)}{\left\{ a + \frac{A}{2} \left[1 - \cos \left(\frac{2\pi z_1}{L}\right) \right] \right\} \left[1 + \left(\frac{A\pi}{L}\right)^2 \sin^2 \left(\frac{2\pi z_1}{L}\right) \right]^{\frac{1}{2}}} \quad (2)$$

is the mean curvature of this interface. In the same manner, Laplace's equation applied to the advancing (right) interface requires

$$P^{(o)} - P_{\text{downstream}}^{(w)} = -2H^{(o,w)} \gamma \quad (3)$$

with the understanding that $P_{\text{downstream}}^{(w)}$ is the pressure in the water downstream of the oil segment and

$$H^{(o,w)} = - \frac{\cos \theta_2 + \left(\frac{A\pi}{L} \right) \sin \theta_2 \sin \left(\frac{2\pi z_1}{L} \right)}{\left\{ a + \frac{A}{2} \left[1 - \cos \left(\frac{2\pi z_2}{L} \right) \right] \right\} \left[1 + \left(\frac{A\pi}{L} \right)^2 \sin^2 \left(\frac{2\pi z_2}{L} \right) \right]^{\frac{1}{2}}} \quad (4)$$

Subtracting Equation (2) from Equation (1), we find

$$\frac{\Delta P a}{2 \gamma} = - \left(a H^{(w,o)} + a H^{(o,w)} \right) \quad (5)$$

after having introduced

$$\Delta P = P_{\text{upstream}}^{(w)} - P_{\text{downstream}}^{(w)} \quad (6)$$

as the pressure drop over the oil segment.

For given values of θ_1 , θ_2 , the volume $V^{(o)}$ of the oil segment, and the pore dimensions a and A , we were able to calculate from Equation (5) $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$. Examples of these computations are shown in Figures 2 through 4. In each case, the maximum value of $\frac{\Delta P a}{2 \gamma}$ is the

critical value below which the oil segment will not be displaced from the pore.

Discontinuous Movements in Single Pore

In carrying out these computations, we observed that some oil globules, either because of their size or because of the magnitudes of their advancing and receding contact angles, can not assume a static configuration at every point in the pore. If we think of an oil segment slowly being displaced through a sequence of static configurations, at some point it might appear to move discontinuously from one configuration to another, because intermediate static configurations fail to exist. Examples of the manners in which discontinuous movement can occur are shown in Figures 5 through 8.

Figure 5 shows a residual oil globule in a sequence of static configurations as it advances from left to right through an oil-wet pore. It appears that some residual oil will be left behind and that the volume of the initial oil segment will be reduced as it moves through the pore. A discontinuous movement of this kind was found in carrying out the computations for Figure 4.

Figure 6 indicates what can happen to a smaller oil segment under oil-wet conditions. It is so small that it can not maintain a static configuration at all positions in the pore. It must rupture, again trapping oil on the boundary of the pore.

We can think of oil being displaced under oil-wet conditions by alternately being spread over the pore walls and then remobilized. Oil-wet conditions appear to be unfavorable for efficient displacement of residual oil.

Figure 7 pictures an oil segment moving from left to right under water-wet conditions. Notice that there will be a discontinuity in its movement

as it passes over the trapped ring of water. This form of discontinuous movement was observed in constructing Figure 2.

In Figure 8, a smaller oil segment is isolated as a spherical drop at one point in the displacement. The remobilization of an isolated spherical drop depends upon other considerations. If the pressure drop over the pore is sufficiently large, the thin aqueous film separating the leading surface of the drop from the pore wall may rupture, allowing the drop to return to the configuration shown in Figure 8A. Alternatively, if the aqueous film is stable, the drop may deform under a sufficiently large pressure drop and squeeze through the neck of the pore, never touching the pore wall. Fortunately, even if the pressure drop over the pore is not sufficiently large to bring either of these mechanisms into play, larger oil segments being swept downstream can coalesce with the smaller isolated spherical drops for an efficient displacement. This suggests that under water-wet conditions everything possible should be done to promote coalescence, for example by reducing the interfacial viscosities.

Haines Jumps

The experimentally observed Haines jumps (Haines 1930, Heller 1968) can be anticipated from the computations of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ examples of which are shown in Figures 2 through 4. In order to illustrate what I mean, let us confine our attention to the conditions for which Figure 3 was constructed and let us assume that the pressure drop across the pore is a little larger than the maximum pressure drop shown there. This means that the residual oil globule will be continuously displaced through the pore.

As the receding (left) interface in Figure 1 moves from $\frac{z_1}{L} = -0.38$ to -0.21 , the oil globule accelerates; the pressure required to hold the globule in a static configuration is continuously reduced as the oil moves forward. Experimentally, this might be seen as a jump.

The globule creeps forward from $\frac{z_1}{L} = -0.21$ to 0.06 , since the pressure required to hold the oil in a static configuration increases sharply as the oil moves to the right. The oil globule might appear to almost pause in contrast with the preceding jump.

Following another jump from $\frac{z_1}{L} = 0.06$ to 0.4 , the oil globule might again creep forward from $\frac{z_1}{L} = 0.4$ to 0.62 .

The discontinuous movements described in the preceding section should be distinguished from the Haines jumps. In some cases, the discontinuous movement of an oil segment may initiate a Haines jump, but the fundamental phenomena seem quite different.

Effect of Oil Segment Volume

The critical value of $\frac{\Delta P a}{2 \gamma}$ required to recover a residual oil globule trapped in a single pore is $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$, the maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ necessary to hold the oil in a static configuration. For given contact angles and for a given pore geometry, $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ is a function of the volume of the oil segment. The functional dependence of $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ upon oil volume will not be smooth because of discontinuous movements.

Table 1 presents $\frac{\Delta P a}{2 \gamma}$ as a function of dimensionless oil volume $V^{(o)}$ for a typical water-wet case, assuming that an oil segment whose volume is less than V_D may not be displaced (see Discontinuous Movements...). Here V_D is the maximum volume of an oil segment that becomes a drop at some point in the displacement (see Figure 8). For oil volumes larger than $(V_D + V_{UP} - V_{CW})$, $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ is a periodic function of oil volume with a period $(V_{UP} - V_{CW})$. By V_{UP} we mean the volume of a pore unit, the volume between $\frac{z_1}{L} = 0$ and 1 in Figure 1; V_{CW} is the volume of the connate water in a pore unit (see Figure 7C).

For intermediate wettabilities, an oil segment whose volume is less than either V_D or V_R may not be displaced (see Discontinuous Movements...). By V_R , we mean the maximum volume of an oil globule that ruptures and is left trapped on the pore wall at some point in the displacement (see Figure 6 as well as Tables 2 and 3). Table 2 gives $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ as a function of dimensionless oil volume for a typical case of intermediate wettability in which V_R happens to be larger than V_D . For the advancing and receding contact angles specified, there is no connate water trapped during the displacement (see Figure 7C). For oil volumes larger than $(V_R + V_{UP})$, $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ is a periodic function of oil volume with a period V_{UP} .

Table 3 gives $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ as a function of dimensionless oil volume for a typical oil-wet case, assuming that an oil segment whose volume is less than V_R may not be displaced (see Discontinuous Movements...). For oil volumes larger than $(V_R + V_{UP})$, $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ is a periodic function of oil volume with a period V_{UP} .

Effect of Wettability

In the absence of better information, we have taken the relationship between the advancing and receding contact angles to be the class III behavior established by Morrow (1974) for roughened polytetrafluorethylene surfaces. Morrow found that the advancing and receding contact angles at these rough surfaces agreed well with the apparent advancing and receding contact angles obtained from capillary pressure data in six different types of consolidated polytetrafluorethylene porous media.

Table 4 presents the maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ for several values of the equilibrium contact angle θ_E . Table 5 gives the maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of both $\frac{z_1}{L}$ and $\frac{v^{(o)}}{a^3}$ for these same values of θ_E .

Tables 4 and 5 indicate that water-wet behavior is preferable for tertiary oil recovery. Notice that oil-wet behavior is preferable to intermediate wettability behavior. A surfactant system that altered wettability by only a small amount could have an adverse effect on oil recovery from an oil-wet system.

Effect of Pore Geometry

Table 6 shows the maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of both $\frac{z_1}{L}$ and $\frac{v^{(o)}}{a^3}$ for several values of $\frac{A}{a}$ and for three typical wettability conditions. With reference to Figure 1, these results show that as the ratio of the bulge radius $(A + a)$ to the neck radius a increases, $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$ also increases.

The effect of changing the core wettability is more significant for small values of $\frac{A}{a}$. This suggests that the alteration of wettability

may be more effective for a low interfacial tension waterflood in a sandstone, which would typically be characterized by a small value of $\frac{A}{a}$ (Batra and Dullien 1973).

Comparison with Experimental Data

Let us assume that a typical residual oil segment extends over 5 pore units and that the unit pore length is 6 times the mean pore neck radius (Dullien et al. 1972; Dullien and Batra 1970; Batra and Dullien 1973; Payatakes et al. 1973). This allows us to estimate the effective length l_e of a single pore as

$$l_e = 30 \bar{a} \quad (7)$$

Using Equation (7), we can say

$$\begin{aligned} \frac{\Delta P \bar{a}}{2 \gamma} &= \left(\frac{\Delta P}{l_e} \right) (30 \bar{a}) \left(\frac{\bar{a}}{2 \gamma} \right) \\ &= 15 \left(\frac{\Delta P}{l} \right) \left(\frac{\bar{a}^2}{\gamma} \right) \left(\frac{l}{l_e} \right) \\ &= \frac{15}{T} \frac{|\nabla P| \bar{a}^2}{\gamma} \end{aligned} \quad (8)$$

with the understanding that l is the distance measured in the direction of gradient over which the pressure drop ΔP occurs

$$|\nabla P| = \frac{\Delta P}{l} \quad (9)$$

and T is the tortuosity

$$T = \frac{l_e}{l} \quad (10)$$

Since Bitterlich and Wobking (1970) report tortuosities for sandstones ranging from 3 to 4, let us choose

$$T = \sqrt{12} \quad (11)$$

The development in Appendix A suggests as an approximation

$$\bar{a} = 4\sqrt{5} \left(\frac{k}{\gamma \psi} \right)^{\frac{1}{2}} \quad (12)$$

This allows us to write Equation (8) as

$$\frac{\Delta P \bar{a}}{2 \gamma} = \frac{600}{\sqrt{3}} \frac{|\nabla P| k}{\gamma \psi} \quad (13)$$

Equation (13) can be used to estimate the critical value of $\frac{|\nabla P| k}{\gamma \psi}$ required for significant oil recovery by saying

$$\left(\frac{|\nabla P| k}{\gamma \psi} \right)_{\text{crit}} = \frac{\sqrt{3}}{600} \left(\frac{\Delta P \bar{a}}{2 \gamma} \right)_{\text{max}} \quad (14)$$

The understanding here is that $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{\max}$ is the critical value of $\frac{\Delta P \bar{a}}{2 \gamma}$ required for the displacement of a residual oil segment from an irregular pore of the form shown in Figure 1. In the absence of more detailed information concerning a particular porous structure, we recommend (Dullien et al. 1972; Dullien and Batra 1970; Batra and Dullien 1973; Payatakes et al. 1973)

$$\frac{A}{a} = 1.5 \quad (15)$$

and

$$\frac{L}{a} = 6.0 \quad (16)$$

With these assumptions and making only general judgements concerning the wettability of the structure, $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{\max}$ can be approximated from Table 6.

The comparisons with data from the literature given in Tables 7 and 8 are made under these conditions.

Table 9 offers estimates from Equation (14) of the critical interfacial tension required in order to recover a significant amount of residual oil, assuming that $|\nabla P| = 0.5 \text{ psi/ft}$ and $\psi = 0.2$. The critical interfacial tension is much more dependent upon permeability than upon wettability.

Conclusions

The static analysis described in the text for the displacement of residual oil from an irregular capillary tube suggests the following.

1. For the most efficient displacement of residual oil, the porous structure should be water-wet.

Figures 5 and 6 indicate that, as residual oil is displaced under oil-wet conditions, it is alternately spread over the pore walls and then remobilized. Table 9 shows that the critical interfacial tension, above which residual oil will not be displaced from the porous medium, is somewhat higher for water-wet behavior. From Table 6, we see that this advantage of water-wet behavior becomes more pronounced as the capillaries more nearly approximate straight circular cylinders (as the ratio of the bulge radius to the neck radius, $\frac{A + a}{a}$ in Figure 1, becomes smaller).

2. Intermediate wettability may be less desirable than either oil-wet or water-wet behavior.

Table 9 indicates that the critical interfacial tension is lower for intermediate wettability behavior than for either oil-wet or water-wet behavior. Table 6 suggests that the disadvantage of intermediate wettability behavior is more significant as the capillaries more nearly approximate straight circular cylinders.

3. Equation (14) may be used together with Table 6 in order to estimate the critical value of $\frac{|\nabla P|}{\gamma} \frac{k}{\mu}$ required for significant recovery of residual oil from sandstones.

Tables 7 and 8 compare estimates made in this manner with the data of Ehrlich et al. (1974), Gale and Sandvik (1973), and Taber et al. (1973). The deviations between the estimated and experimental values, which are generally less than 50%, are attributable in part to the assumptions required concerning experimental conditions.

Appendix A: Estimation of Pore Neck Radius

For steady-state, laminar flow through a circular pipe,

$$v = \frac{\Delta P R^2}{8 \mu \ell_e} \quad (A1)$$

where v is the area-averaged axial component of velocity, ΔP is the pressure drop, R is the radius of the pipe, μ is the viscosity of the fluid, and ℓ_e is the length of the pipe. If the pipe is not circular, we can write by analogy with Equation (A1)

$$v = \frac{\Delta P R_h^2}{k_o \mu \ell_e} \quad (A2)$$

Here R_h is the hydraulic radius of the pipe, which is defined as the cross sectional area available for flow divided by the wetted perimeter; k_o is a shape factor, values of which have been tabulated for various cross sections by Carman (1937).

If we are concerned only with flow in one direction, a simple model for a porous medium is a bundle of capillaries that have a mean hydraulic radius $\bar{R}_h$ and a mean cross sectional area $\bar{A}_c$. The volume rate of flow through a single pore may be described by

$$\bar{A}_c v = \frac{\bar{A}_c \Delta P \bar{R}_h^2}{k_o \mu \ell_e} \quad (A3)$$

If N is the number of pores in the structure, then

$$N = \frac{\psi A}{A_c T} \quad (A4)$$

with the understanding that ψ is the porosity, A is the cross sectional area of the porous structure measured normal to the direction of flow, and ℓ is the distance measured in the direction of pressure gradient over which the pressure drop ΔP occurs. The total volume rate of flow Q through the structure is consequently

$$\begin{aligned} Q &= N A_c v \\ &= \left(\frac{A \Delta P}{\mu \ell_e} \right) \left(\frac{\ell}{\ell_e} \right) \left(\frac{\psi R_h^2}{k_o} \right) \end{aligned} \quad (A5)$$

From Darcy's law,

$$Q = \frac{A k \Delta P}{\mu \ell} \quad (A6)$$

where k is the permeability of the structure. Eliminating Q between Equations (A5) and (A6), we find

$$R_h = \left(\frac{k k_o}{\mu} \right)^{\frac{1}{2}} T \quad (A7)$$

The tortuosity T is defined by Equation (10). If we interpret each pore to be a circular tube, Equation (A7) may be expressed in terms of the mean pore radius $\bar{R}$:

$$\begin{aligned} R &\equiv .2 \bar{R}_h \\ &= 2 \left(\frac{k k_o}{\psi} \right)^{\frac{1}{2}} T \end{aligned} \quad (A8)$$

From the analysis by Payatakes et al. (1973) of steady-state incompressible newtonian flow through a periodically constricted tube, we will say

$$\frac{\bar{R}}{a} = \sqrt{1.5} \quad (A9)$$

On the basis of the data by Wyllie and Spangler (1952) for consolidated sandstones, we choose

$$k_o = 2.5 \quad (A10)$$

Equations (11), (A9), and (A10) can be used to rearrange Equation (A8) in the form of an estimate for $\bar{a}$, Equation (12).

Batra and Dullien (1973) have reported $\bar{a}$, k , and ψ for 15 sandstone cores. Equation (12) is compared with their data in Table 10.

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Table 1: Maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ for several values of $\frac{v^{(o)}}{a^3}$ assuming a typical water-wet behavior.

$$\frac{A}{a} = 1.5 \quad \frac{L}{a} = 6.0$$

$$\theta_1 = 40^\circ \quad \theta_2 = 4^\circ$$

$\frac{v^{(o)}}{a^3}$	$\left(\frac{\Delta P a}{2 \gamma} \right)_{\max}$
46.00*	0.323
50	0.676
56.48	0.884**
60	0.755
70	0.523
80	0.431
90	0.376
100	0.339
105.42***	0.323

* v_D

** maximum value of $\left(\frac{\Delta P a}{2 \gamma} \right)_{\max}$

*** $(v_D + v_{UP} - v_{CW})$

Tables 2: Maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ for several values of $\frac{v^o}{a^3}$ assuming a typical intermediate wettability behavior.

$$\frac{A}{a} = 1.5$$

$$\frac{L}{a} = 6.0$$

$$\theta_1 = 140^\circ$$

$$\theta_2 = 38^\circ$$

$\frac{v^{(o)}}{a^3}$	$\left(\frac{\Delta P a}{2 \gamma}\right)_{\max.}$
10.16*	1.52
20	1.41
30	1.34
40	1.38
50	1.48
60	1.69
62.91	1.75**
70	1.59
73.19***	1.52

* v_R

** maximum value of $\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$

*** $(v_R + v_{UP})$

Table 3: Maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ for several values of $\frac{v^{(o)}}{a^3}$ assuming typical oil-wet behavior.

$$\frac{A}{a} = 1.5$$

$$\frac{L}{a} = 6.0$$

$$\theta_1 = 175^\circ$$

$$\theta_2 = 130^\circ$$

$$\frac{v^{(o)}}{a^3}$$

$$\left(\frac{\Delta P a}{2 \gamma} \right)_{\max}$$

32.21*	0.557
40	0.513
50	0.594
60	0.776
68.88	0.979**
70	0.978
80	0.854
90	0.604
95.24***	0.557

* v_R

** maximum value of $\left(\frac{\Delta P a}{2 \gamma} \right)_{\max}$

*** $(v_R + v_{UP})$

Table 4: Maximum values of $\frac{\Delta P a}{2 \gamma}$ as a function of $\frac{z_1}{L}$ for several values of θ_E assuming Morrow's (1974) class III contact angle hysteresis.

$$\frac{A}{a} = 1.5 \quad \frac{L}{a} = 6.0$$

$$\frac{V^{(o)}}{a^3} = 80.0$$

θ_E^* (degrees)	θ_1^* (degrees)	θ_2^* (degrees)	$\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$
24	10	0	0.381
30	20	2	0.387
40	40	4	0.437
49	60	7	0.637
59	80	11	0.870
69	100	14	1.11
79	120	21	1.31
89	140	38	1.44
100	160	64	1.42
117	170	90	1.25
137	175	130	0.853
150	178	160	0.544
156	180	170	0.534

* θ_E : Equilibrium contact angle measured through the aqueous phase.

θ_1 : Advancing contact angle measured through the aqueous phase.

θ_2 : Receding contact angle measured through the aqueous phase.

Table 5: Maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of both $\frac{z_1}{L}$ and $\frac{V^o}{a^3}$ for several values of θ_E assuming Morrow's (1974) class III contact angle hysteresis.

$$\frac{A}{a} = 1.5 \qquad \frac{L}{a} = 6.0$$

θ_E^* (degrees)	θ_1^* (degrees)	θ_2^* (degrees)	$\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$
24	10	0	0.659
30	20	2	0.725
40	40	4	0.884
49	60	7	1.08
59	80	11	1.28
69	100	14	1.50
79	120	21	1.68
89	140	38	1.75
100	160	64	1.64
117	170	90	1.40
137	175	130	0.979
150	178	160	0.721
156	180	170	0.664

* θ_E : Equilibrium contact angle measured through the aqueous phase.

θ_1 : Advancing contact angle measured through the aqueous phase.

θ_2 : Receding contact angle measured through the aqueous phase.

Table 6: Maximum value of $\frac{\Delta P a}{2 \gamma}$ as a function of both $\frac{z_1}{L}$ and $\frac{v(o)}{a^3}$ for several volumes of $\frac{A}{a}$ and for three typical wettability conditions.

$$\frac{L}{a} = 6.0$$

$\frac{A}{a}$	$\left(\frac{\Delta P a}{2 \gamma}\right)_{\max}$		
	$\theta_1 = 40^\circ$ $\theta_2 = 4^\circ$ (water-wet)	$\theta_1 = 140^\circ$ $\theta_2 = 38^\circ$ (intermediate)	$\theta_1 = 170^\circ$ $\theta_2 = 130^\circ$ (oil-wet)
0.0*	0.232	1.55	0.353
0.5	0.558	1.65	0.667
1.0	0.756	1.71	0.859
1.5	0.884	1.75	0.979
2.0	0.957	1.78	1.05
2.5	1.00	1.80	1.10
3.0	1.03	1.82	1.14

* Straight cylinder.

Table 7: Equation (14) compared with data of Ehrlich et al. (1974) and of Gale and Sandvik (1973).

Authors	Ehrlich et al. (1974)	Ehrlich et al. (1974)	Ehrlich et al. (1974)	Gale and Sandvik (1973)	Gale and Sandvik (1973)
Sandstone	Berea	Jelm No. 1	Jelm No. 2	Berea	Berea
Oil Phase	Mineral Oil	Mineral Oil	Mineral Oil	Borregos Crude Oil	Borregos Crude Oil
Water Phase	2% NaCl Brine	2% NaCl Brine	2% NaCl Brine	2% Surfact: Solution (SO ₃ -Feed C)	2% Surfact. Solution (20% Oleum Blend)
Permeability k (millidarcies)	230	1,014	491	150	150
Porosity, ψ (fraction)	0.200	0.229	0.199	0.2*	0.2*
Initial Res. Oil Sat. (%)	31.3	31.5	29.0		
% of Res. Oil Recovery	50	50	50	70	44
$ \nabla P $ (psi/ft)	3,250	780	1,560	1.0	1.0
γ (dynes/cm)	40.0	40.0	40.0	0.005	0.01
$\frac{ \nabla P k}{\gamma \psi}$	2.08×10^{-3}	1.93×10^{-3}	2.14×10^{-3}	3.35×10^{-3}	1.67×10^{-3}
$\left(\frac{ \nabla P k}{\gamma \psi}\right)^{**}_{crit.}$	2.55×10^{-3}	2.55×10^{-3}	2.55×10^{-3}	2.55×10^{-3}	2.55×10^{-3}

* Assumed Values.

** Calculated from Equation (14) with $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{max}$ taken from Table 6 for $\frac{A}{a} = 1.5$ and water-wet behavior.

Table 8: Equation (14) compared with data of Taber et al. (1973)

Core No.	Core Type	Permeability, k (m. d.)	Porosity ψ (fract.)	Initial Resid. Oil Sat. (%)	% Recovery of Resid. Oil	$\frac{ \nabla P }{\gamma}$	$\frac{ \nabla P k}{\gamma \psi}$	$\left(\frac{ \nabla P k}{\gamma \psi}\right)_{crit.}^*$
ON-12	- - -	320	0.183	33.0	28.2	86.7	3.38×10^{-3}	2.55×10^{-3}
Ber-1	Berea	346	0.191	40.5	25.1	46.2	1.87×10^{-3}	2.55×10^{-3}
SP-5	St. Peters	613	0.231	48.6	27.2	30.9	1.83×10^{-3}	2.55×10^{-3}
DOT	- - -	635	0.299	32.1	29.8	21.5	1.02×10^{-3}	2.55×10^{-3}
21X	Berea	752	0.216	45.3	26.4	30.9	2.40×10^{-3}	2.55×10^{-3}
80	- - -	1,450	0.144	49.7	34.1	24.2	5.43×10^{-3}	2.55×10^{-3}
MG-6	- - -	2,190	0.166	49.3	48.2	12.2	3.58×10^{-3}	2.55×10^{-3}

* Calculated from Equation (14) with $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{max}$ taken from Table 6 for $\frac{A}{a} = 1.5$ and water-wet behavior.

Table 9: Critical interfacial tension required to recover a significant amount of residual oil.

k (millidarcies)	* γ_{crit} (dyne/cm)		
	$\theta_1 = 40^\circ$ $\theta_2 = 4^\circ$ (Water-wet) $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{max} = 0.884$	$\theta_1 = 140^\circ$ $\theta_2 = 38^\circ$ (Intermediate) $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{max} = 1.75$	$\theta_1 = 175^\circ$ $\theta_2 = 130^\circ$ (Oil-wet) $\left(\frac{\Delta P \bar{a}}{2 \gamma}\right)_{max} = 0.97$
10	2.2×10^{-4}	1.1×10^{-4}	2.0×10^{-4}
100	2.2×10^{-3}	1.1×10^{-3}	2.0×10^{-3}
1000	2.2×10^{-2}	1.1×10^{-2}	2.0×10^{-2}

* γ_{crit} : Estimated from Equation (14) assuming $|\nabla P| = 0.5$ psi/ft.
and $\psi = 0.2$.

Table 10: Comparison of measured values of $\bar{a}$ from Batra and Dullien (1973) with estimates from Equation (12).

Sample	k millidarcies	ψ	$\bar{a}$ (μ) measured	$\bar{a}$ (μ) estimated	Per cent* Deviation
Belt Series	0.36	0.0830	0.22	0.585	166.0
Squirrel	26	0.2375	1.0	2.94	194.0
Whetstone	0.75	0.1340	1.05	0.665	-36.7
Bandera	10	0.191	2.5	2.03	-18.8
Noxie	205	0.2825	4.25	7.57	78.1
Clear Creek	78	0.1908	4.00	5.68	42.0
Big Clifty	132	0.1922	4.50	7.36	63.6
Torpedo	252	0.2457	5.00	9.00	80.0
Cottage Grove	116	0.2159	5.50	6.51	18.4
St. Meinrad	210	0.2474	7.05	8.19	16.2
Berea	233	0.1780	13.0	10.2	-21.5
Noxie	298	0.2503	12.0	9.70	-19.2
Berea	268	0.2950	11.25	8.47	-24.7
Boise	1,180	0.2316	23.5	20.1	-3.6
Bartsville	988	0.2141	13.5	19.1	41.5

* $(\text{estimated } \bar{a} - \text{measured } \bar{a}) / (\text{measured } \bar{a})$.

Figure 1: The model pore containing a segment of residual oil.

Displacement is from left to right.

Figure 2: The pressure drop required to hold a segment of residual oil in a static configuration as a function of the position of its receding (left) interface in Figure 1 for typical water-wet behavior. In region A, the receding interface can not touch the pore wall because of the discontinuous movement illustrated in Figure 7C.

Figure 3: The pressure drop required to hold a segment of residual oil in a static configuration as a function of the position of its receding (left) interface in Figure 1 for typical intermediate wettability behavior.

Figure 4: The pressure drop required to hold a segment of residual oil in a static configuration as a function of the position of its receding (left) interface in Figure 1 for typical oil-wet behavior. In region B, the receding interface can not touch the pore wall because of the discontinuous movement shown in Figure 5c.

Figure 5: Sequence of static configurations as an oil segment moves through an oil-wet pore, leaving a portion of itself behind trapped on the wall.

Figure 6: A smaller oil segment can not assume a static configuration at all positions in an oil-wet pore. It will be trapped on the wall of the pore.

Figure 7: Sequence of static configurations as an oil segment moves through a water-wet pore over a trapped ring of connate water.

Figure 8: A small oil segment may be trapped in the form of a spherical drop as it is displaced through a water-wet pore.

Objective B: The Measurement of Small Interfacial Tensions by the Rod-In-Free Surface Meniscal Breakoff Method. (D. Yannimaras and A. A. Kovitz)

This quarter (December 1, 1975 through February 29, 1976) saw the completion of Version II of the Meniscal Breakoff Instrument (see Quarterly Technical Progress Letter for September 1, 1975 to November 30, 1975, ERDA Contract No. E(34-1)-0019, December 1975). The device appears to be satisfactory in its overall operation but still lacks the ability to produce reliable, precise data with known error limits. This conclusion is based upon preliminary observations of the system's satisfactory behavior with water-air and extrapolation of that behavior to low-tension systems; no low-tension measurements have, as yet, been attempted.

The reasons for current difficulties and, therefore, slower progress than anticipated are considered to be as follows:

- a) translation of the interface by manual actuation of the micrometer or differential screw results in non-uniform, non-repeatable motion of the interface and emerging meniscus;
- b) the solidity and stiffness of the instrument's structural framework is not suitable when considering translations as small as 10^{-5} cm. These considerations are not important under ordinary circumstances; their influence for low-tension systems is crucial.

The past month has been devoted to design of a Version III of the meniscal breakoff instrument. It will incorporate the motorized articulation of a differential screw for translation of the interface; in this way the time to meniscal breakoff will be made to be of the order of hours rather than minutes, and the motion will be uniform and repeatable. A automatic shut off at breakoff is also part of the design. The instruments' structural framework is also being altered to assure the required stiffness for reliable resolution of measurements in the 10^{-5} cm range; if building vibrations become a problem the apparatus will be moved to a vibration isolated pad available in the basement of the institute.

Although faster progress could have been achieved by using the Version II instrument, it is felt that the time spent now in design and construction of Version III is, in the long run, a better plan.

Numerical Computations

It was noted in the last Quarterly Technical Progress Letter (September 1, 1975 to November 30, 1975) that further computations and calculations relating to meniscus volume were being initiated. These calculations are now complete. They will provide a more complete theory of the instrument, particularly for interfaces of moderate tension.