CHAPTER V
RECOVERY OF CRUDE OIL FROM CORE SAMPLES BY LOW AND HIGH CONCENTRATION SURFACTANT FLOODING

The ultimate objective of development of surfactant system is their application for the recovery of oil from the porous medium. For this purpose, simulated laboratory tests (flooding tests) are done on the core samples obtained from the oil reservoirs. In order to determine the ideal mode for the field, two types of laboratory simulated tests are done, viz. low concentration, high pore volume surfactant flooding (Micelle Flooding) or high concentration, low pore volume surfactant flooding (Microemulsion Flooding). In the former method about 15-60 p.c. pore volume of a surfactant slug is injected whereas in the latter only 3-20 p.c. pore volume of surfactant slug is used for flooding. Low concentration surfactant flooding is an immiscible type of flooding, whereas the high concentration flooding may be immiscible or miscible depending upon the solubility of the residual oil in the flooding medium. If the microemulsion slug is of the oil-external type, oil is miscible in all
properties, and a miscible type of flood will result \(^1\). In the miscible type of microemulsion flooding, surfactant adsorption on the rock as well as mixing with brine and oil at the front and with polymer-water (from mobility) at the rear, cause gradual deterioration of the bank. Eventually, even the highest surfactant concentration present in the bank will fall below the multiphase boundary, one or more phases will break out and therefore displacement assumes an immiscible character \(^2\).

In recent years both the types of floods are extensively studied in the laboratory and in the field. Several authors \(^3\)-\(^6\) related the term 'process efficiency' to the ratio of oil recovered to the amount of surfactant injected. Displacement results from three different laboratories as reported by Gale and Sandvik \(^4\), Hill et al \(^5\) and Davis and Jones \(^6\) are presented in Table 1. All floods were carried out on Berea cores and used petrolous sulphonates as surfactant. Floods 1 and 2 are indicative of low concentration whereas flood 3 is representative of a high concentration, small pore volume flood. Polymer solution was used for mobility control in floods 2 and 3 only. The high recovery in 2 in comparison to 1 may also be due to the
The use of mobility control buffer.

**Table 1.**

<table>
<thead>
<tr>
<th>Flood No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant conc.   (p.c.)</td>
<td>2</td>
<td>1.3</td>
<td>10.4</td>
</tr>
<tr>
<td>Pore volume injected (p.c.)</td>
<td>50</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Core dim. (in. x ft)</td>
<td>2x3</td>
<td>2x16</td>
<td>2x4</td>
</tr>
<tr>
<td>Rate/Pressure</td>
<td>3 p.s.i.</td>
<td>1.4 ft/D</td>
<td>4 ft/D</td>
</tr>
<tr>
<td>Tertiary oil recovery</td>
<td>70</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Efficiency</td>
<td>0.70</td>
<td>2.62</td>
<td>4.09</td>
</tr>
</tbody>
</table>

But the other parameters such as pore volume, oil saturation, connate water content, porosity, permeability, mobility control must also be taken into account in evaluation of the efficiency of oil recovery processes.
Physical properties of core samples relevant to oil recovery

The extent of entrapment and release of oil is intimately related to three physical properties of rocks which have been frequently mentioned before. The properties are porosity, pore volume and permeability. A knowledge of porosity and permeability of an oil reservoir rock is essential to estimate its fluid content, rate of flow and possible oil recovery.

Porosity

Porosity is a measure of void space within a rock sample expressed as a fraction (or percentage) of the bulk volume of that rock. The general expression for porosity is,

\[ \phi = \frac{V_b - V_s}{V_b} = \frac{V_p}{V_b} \]  

(1)

Where \( \phi \) = porosity, 
\( V_b \) = bulk volume of rock, 
\( V_s \) = net volume occupied by solids (also called grain volume) and 
\( V_p \) = pore volume = the difference between bulk and solid volumes.
In actual rocks, porosity is also classified as,
(a) absolute porosity which is the total porosity
of a rock, regardless of whether or not the
individual voids are connected and (b) effective
porosity, which is only that porosity due to voids
which are inter connected. It is the effective
porosity which is of interest to the oil industry.
But in the case of laboratory flooding, effective
and absolute porosities are same.

It may be deduced from equation (1) that
porosity of a sample can be determined from a
knowledge of any two of the factors from $V_p$, $V_g$ or
$V_p$. There are several ways by which these may be
measured with reasonable accuracy.7

The grain volume can be determined from the
dry weight of the sample and the sand-grain density.
For most processes sufficiently accurate results
can be obtained by using the density of quartz
(2.65 g/cm$^3$) as the sand-grain density.8

For more accurate determinations, the
Mellighan, Nutting or Russell's methods can be used.9
In both the cases, the bulk volume is determined
and then either that sample or an adjacent sample is reduced to grain size, and then the grain volume is determined. In Malicher-Nutting technique all the measurements are done gravimetrically, utilizing the principle of buoyancy. Whereas in the Russell method a specially designed volumeter is used to determine the bulk and grain volumes volumetrically. The porosity determined here is the total porosity.

But the most commonly used instruments to be determine the grain volume, are the different types of porosimeters, most of which are based on Boyle's Law Principle. In this method, the difference in the height of the mercury column obtained by lowering and raising the mercury column using a core sample is compared with that obtained by using a substance having a known grain volume.

**Pore volume**

Pore volume of a sample may be measured gravimetrically by saturating the sample with a liquid of known density, and noting the increase in weight. In practice, a high vacuum is created
inside the flask which contains the clean, dry and previously weighed core sample. A liquid such as kerosine or a similar hydrocarbon is allowed to enter the flask (and hence the pores of the core sample) until it completely covers the sample. The saturated sample is then removed from the flask with a forceps, dried of excess liquid and quickly weighed. The pore volume is determined from

\[
V_p = \frac{W_s - W_d}{\rho_t}
\]

where, \(W_s\) is the saturated sample weight, \(W_d\) is the sample weight and \(\rho_t\), the density of the saturating liquid.

Another widely used pore volume determination utilizes the fluid content of the core sample as it comes from the field. In this method a sample of approximately 20 to 30 c.c. bulk volume is used. Mercury is injected into the sample at a relatively high pressure and the injected volume is taken as the volume of gas space \(V_g\) existing in the core. Water or oil contents are then determined by
distillation. The sum of these three fluid volume
vis. $V_g + V_o + V_w$, is the pore volume of the sample.

**Bulk Volume**

Bulk volume of a sample is normally found by the measurement of the volume of liquid it displaces. If the liquid is the one which readily penetrates the pores, the sample must first be saturated with that liquid so that the true bulk volume is displaced. To avoid this problem, mercury is commonly used as the displacing fluid since it will not appreciably penetrate normal pore sizes at low pressures. To keep the pressure low requires, of course, that submergence of the sample be restricted to shallow depths (2-5 cm.). If the sample is a uniform cube or cylinder, its volume may be calculated from its dimensional measurements.

**Permeability**

Permeability is the ability of a fluid to flow through a substance and is interrelated to porosity. For a given pressure difference the rate of flow is proportional to the permeability. The unit for permeability is 'darcy' and is defined as, that,
when one millilitre per second of a fluid of unit viscosity (in centipoise) will flow through a section of 1 cm. length and one square cm. cross section when pressure differential on the opposite faces is one atmosphere (760 mm of mercury). But as this unit 'darcy' was found to be too large, one thousandth of this unit viz. milidarcy is generally used.

The specific permeability of a sample of reservoir rock is usually determined in the laboratory by extracting oil, water or gas from its pore space with a solvent and drying it thoroughly to remove the solvent. Air, oil or water is then forced through it in a permeameter which applies a certain controlled pressure differential across the core and measures the rate of flow through a unit length and unit cross sectional area of the specimen. Substitution of the values in the D'Arcy's formula gives the permeability of the specimen and the results are expressed in milidarcys. The appropriate form of D'Arcy formula for air or gas permeability is,

\[ K = \frac{2 q_2 \mu L}{A (p_1^2 - p_2^2)} \]  

(2)
\[ K = \frac{q_m \mu L}{A \Delta p} \]

Where \( K \) = permeability, (darcys),  
\( q_2 \) = flow rate at exit condition  
\( (cc/sec.) \)  
\( q_m \) = flow rate at mean conditions  
\( \frac{P_1 - P_2}{2} \) (cc/sec.)  
\( \mu \) = gas viscosity at test temperature, (cp.).  
\( L \) = sample length, (cm.).  
\( A \) = sample area, (sq. cm.).  
\( \Delta p \) = pressure differential across sample (atm.).  
\( P_1 \) = inlet pressure, (atm. absolute)  
\( P_2 \) = exit pressure, (atm. absolute)

In the whole core analysis, the procedure for permeability measurement is different. Normally the horizontal permeability is of interest, however vertical permeability may also be desired. Radial flow tests are sometimes performed by boring a vertical hole down the centre of the core through which gas is then allowed to flow.
Relative permeability

Water wet mineral surfaces and water filled pore spaces will permit passage of water but very little of oil and conversely, oil saturated portions of the reservoir will permit passage of oil only but very little of water. Gas will at times flow through and take possession of drainage channels, particularly restricting flow of oil and water. Thus the percentage of each fluid that may move through the different cross sections of the reservoir will vary widely. So, the amount of each component reaching a well will depend upon the amounts of gas, oil and water present in the rock through which flow occurs and this is known as the relative permeability.

In the present work both low and high concentration surfactant flooding is carried out on the core samples described below. Flooding method consisted of injection of a surfactant slug to the residual oil left in the core after a water flooding followed by the injection of polymer slug solution.
Experimental

The flooding apparatus consisted of a core chamber and two separate reservoirs for the storage of oil and water/surfactant slug respectively. The core chamber is of 10 cm. in length and 2.5 cm. internal diameter. Pressures can be measured at a junction near the inlet of the core sample with a pressure transducer as shown in Fig. 1.

The physical characteristics of oil used in the flooding experiments are same as those discussed in chapter IV (table 7) used for interfacial tension determination.

In all the experiments, Dow Pusher 700 (Dow Chemical Co.; partially hydrolyzed polyacrylamide) is used as the mobility buffer. In each flooding experiment 40% IV of the polymer slug is taken for mobility control unless otherwise specified.

Preparation of the core sample

Core sample was of Tipam origin sandstone obtained from an oil reservoir of one of the Assam Oil fields from a depth of 250-2511 metres. The
core sample is thoroughly cleaned and dried at 100°C in a vacuum oven for two hours. It is then cut into appropriate dimension of length (10 cm.) and diameter (2.5 cm.).

**Determination of porosity**

To determine the porosity other related parameters such as pore volume and bulk volume of the core sample are determined first.

**Pore volume**

In the present work pore volume is determined by the saturation method. The weight of the clean and dry core sample is taken. Then it is kept in an assembly as shown in figure 2. Kerosine oil is allowed to enter the vessel until it covers the sample completely. The weight of the 100 p.c. \( K_{oil} \) saturated sample is then taken quickly. The pore volume is determined by the difference in weight of the \( K_{oil} \) saturated core and that of the clean core divided by the density of \( K_{oil} \) used.

**Bulk volume**

Bulk volume is determined by the measurement
Fig II Saturation apparatus for pore volume determination.
of the geometry of its size.

Porosity (p.c.) is calculated by equation 1.
Porosity (p.c.) for the tipam core sample used in this work is found to be 34.7.

Determination of permeability

The absolute permeability is determined from flow test data. The core sample is placed on an assembly fitted with a mercury manometer on one side and water manometer on the other side of the core chamber as shown in figure 3. Air is used as the flowing fluid. The pressure differential is measured by manometers and the flow volume by a gas flow meter. Permeability is calculated by equation (2).

Fluid saturation and surfactant flooding

Core sample is saturated 100 p.c. with water and placed in the core chamber as shown in figure 1. It is then flooded with an excess volume of oil at 20 p.s.i. Water is displaced from the core and is collected in a suitable graduated cylinder or burette. Volume of excess oil coming out is also recorded.
Fig III Apparatus for routine air permeability determinations
After a certain time, the displaced water volume becomes constant and this is taken as irreducible water saturation. From these measurements water and oil saturation in the core sample are calculated before the water flooding. The core is then subjected to water flooding by injection of water at the same pressure (20 p.s.i.), until it comes to an irreducible value. The volume of oil displaced as well as excess water coming out are recorded. This experiment gives the values of oil ($S_{0_r}$) and water ($S_{0_w}$) saturations before surfactant flooding. Now the core is ready for the surfactant flooding. Surfactant slug solution is injected at 20 p.s.i. to the core sample followed by the polymer slug solution. The details of the experiments are discussed below.

**Low concentration surfactant flooding**

Two promising synthetic alkyl benzene sulphonates namely, sodium 1-isopropyl, 4-decyl benzene sulphonate and 1-methyl 4-dodecyl benzene sulphonate are used for surfactant flooding. Preparation of the surfactant slug and the determination of interfacial tensions are already discussed in chapter IV (table 3(a)).
20% pore volume of surfactant slug is injected to the core sample at a pressure of 80 p.s.i., followed by 40% pore volume of polymer slug solution with a frontal velocity of 30 ft/day.

Table 1 shows the effect of surfactant concentration on the recovery of oil using 1-isopropyl 4-decyl benzene sulphonate. It is observed that maximum recovery of oil is coincided with the minimum interfacial tension (0.045 dynes/cm.) at 0.5 p.o. surfactant concentration.

Table 2 shows the effect of sodium chloride concentration in the recovery of oil using 1-isopropyl 4-decyl benzene sulphonate. Here also it is observed that maximum recovery (70 p.o.) corresponds to the lowest interfacial tension (0.045 dynes/cm.) at 2 p.o. sodium chloride concentration.

Effect of the size of the surfactant slug on the recovery of crude oil is also studied. Surfactant slug consisted of 0.5 p.o. of 1-methyl, 4-dodecyl benzene sulphonate containing 2 p.o. sodium chloride and 2 p.o. isobutyl alcohol. Interfacial tension
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Surfactant slug comp.</th>
<th>Interfacial tension (Sv/cm)</th>
<th>Porosity (%) of core sample</th>
<th>Initial oil saturation (S_i) before surf. flood (%)</th>
<th>Water saturation (S_w) before surf. flood (%)</th>
<th>Oil recovered (p.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.065</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.045</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>0.054</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.05</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>0.12</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>32</td>
</tr>
</tbody>
</table>

Surfactant slug solution (20%, v/v) is injected followed by a polymer slug solution (40% PV)
### TABLE 2

**DEPENDENCE ON OIL RECOVERY ON ELECTROLYTE CONCENTRATION**

*Surfactant Slug (1.)*

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Sodium 1-isopropyl 4-decyl benzenesulphonate (p.p.m.)</th>
<th>Sodium Chloride (p.p.m.)</th>
<th>Iso-Butyl Alcohol (p.p.m.)</th>
<th>Interfacial Tension (dy/cm)</th>
<th>Porosity (%) of Core Sample</th>
<th>Initial Oil Saturation (S_i) before Suf. Flood (p.p.u.)</th>
<th>Water Saturation (S_w) before Suf. Flood (p.p.u.)</th>
<th>Oil Recovered (p.p.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>0.14</td>
<td>34.7</td>
<td>40</td>
<td>46.5</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1.5</td>
<td>2</td>
<td>0.05</td>
<td>34.7</td>
<td>40</td>
<td>46.5</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>0.04</td>
<td>34.7</td>
<td>40</td>
<td>46.5</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>3</td>
<td>2</td>
<td>0.05</td>
<td>34.7</td>
<td>40</td>
<td>46.5</td>
<td>46</td>
</tr>
</tbody>
</table>

Surfactant slug solution (20% IV) is injected followed by a polymer slug solution (40% IV).
between oil and the surfactant slug is 0.0068 dynes/cm. Surfactant slug is injected at the same rate as above (30 ft/day) and at the same pressure (20 p.s.i.). Like in the previous case here also each injection of surfactant slug solution is followed by 40 pore volume of polymer solution. Figure 4 and table 3 indicate that on increasing the size of the surfactant slug, recovery increased to a value and then became almost constant, even on further injection of surfactant slug. It is noted that 80 p.c. of oil is recoverable by injecting a 30% pore volume of slug solution. But on further increasing the size of the surfactant slug to 100% pore volume, the increase in the recovery of oil is only 36.3 p.c.

**High concentration surfactant flooding**

High concentration surfactant or microemulsion flooding is studied with dodecyl benzenes sulphonate solution. The preparation of the microemulsion is already discussed in chapter IV (table 12 and 13). After water flooding, 6% pore volume of microemulsion slug is injected to the core sample followed by 36% pore volume of polymer slug.
### TABLE 3

**DEPENDENCE OF OIL RECOVERY ON SURFACTANT SLUG SIZE.**

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Interfacial tension (dy/cm)</th>
<th>Porosity (p.c.) of core sample</th>
<th>Initial oil saturation ($S_{oi}$) before surf. flood (% pv)</th>
<th>Water saturation ($S_{ow}$) before surf. flood (% pv)</th>
<th>Surfactant slug soln. injected (% pv)</th>
<th>Oil recovered (p.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>77.2</td>
</tr>
<tr>
<td>3</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>80.0</td>
</tr>
<tr>
<td>4</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>82.0</td>
</tr>
<tr>
<td>5</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>84.8</td>
</tr>
<tr>
<td>6</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>85.2</td>
</tr>
<tr>
<td>7</td>
<td>0.0068</td>
<td>34.7</td>
<td>42</td>
<td>47</td>
<td>10</td>
<td>86.6</td>
</tr>
</tbody>
</table>

Surfactant is formulated into a slug solution having sodium 1-methyl, 4-dodecyl benzene sulphonate (0.5 p.c.) iso-butyl alcohol (2 p.c.) and sodium chloride (2 p.c.)
Fig. 4 The effect of surfactant slug size on recovery of crude oil.
Table 4 shows the effect of cosurfactant concentration on microemulsion solution and on the recovery of oil. It is found that a microemulsion slug having an optimum cosurfactant concentration gives the low interfacial tension and higher recoveries of oil.

Figure 5 and table 5 shows the effect of sodium chloride concentration on microemulsion solution and on the recovery of crude oil. It is also noted that at optimum sodium chloride concentration only, maximum amount of oil is recovered.
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Surfactant slug comp.</th>
<th>Interf. tension (dy/cm)</th>
<th>Permeability (% of the core sample)</th>
<th>Initial oil saturation ($S_{oi}$) before surf. flood (% pv)</th>
<th>Water saturation ($S_{ow}$) before surf. flood (% pv)</th>
<th>Oil recov. (% to $S_{oi}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 1 4 2.5</td>
<td>0.12</td>
<td>34.7</td>
<td>44</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>6 1 6 7.5</td>
<td>0.091</td>
<td>34.7</td>
<td>44</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>6 1 8 11</td>
<td>0.06</td>
<td>34.7</td>
<td>44</td>
<td>45</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>6 1 9 6.2</td>
<td>0.105</td>
<td>34.7</td>
<td>44</td>
<td>45</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>6 1 10 6</td>
<td>0.115</td>
<td>34.7</td>
<td>44</td>
<td>45</td>
<td>25</td>
</tr>
</tbody>
</table>

Microemulsion (6 %v) is injected followed by a polymer slug (36 p. o. pv).
TABLE 5

DEPENDENCE OF OIL RECOVERY ON ELECTROLYTE CONCENTRATION

IN MICROEMULSION SLUG.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Surfactant slug comp.</th>
<th>Interf. tension (dy/cm)</th>
<th>Porosity (%) of the core sample</th>
<th>Initial oil saturation ($S_{o}$) before surf. flood (%)</th>
<th>Water saturation ($S_{w}$) before surf. flood (%)</th>
<th>Oil recov. (%) to $S_{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium dodecyl benzene sulphonate (p.c.) 6</td>
<td>0.2</td>
<td>8</td>
<td>1</td>
<td>0.12</td>
<td>34.7</td>
</tr>
<tr>
<td>2</td>
<td>Sodium chloride (p.c.) 6</td>
<td>0.4</td>
<td>8</td>
<td>3</td>
<td>0.11</td>
<td>34.7</td>
</tr>
<tr>
<td>3</td>
<td>Isobutyl alcohol (p.c.) 6</td>
<td>0.8</td>
<td>8</td>
<td>7</td>
<td>0.091</td>
<td>34.7</td>
</tr>
<tr>
<td>4</td>
<td>Crude oil dissolv. (p.c.) 6</td>
<td>1.0</td>
<td>8</td>
<td>11</td>
<td>0.06</td>
<td>34.7</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>1.2</td>
<td>8</td>
<td>6</td>
<td>0.085</td>
<td>34.7</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>1.6</td>
<td>8</td>
<td>4</td>
<td>0.091</td>
<td>34.7</td>
</tr>
</tbody>
</table>

Microemulsion slug (6 % PV) is injected followed by a polymer slug solution (36 % PV).
Fig. 5. The effect of sodium chloride on recovery of crude oil.

The effect of sodium chloride on interfacial tension.
References


