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IN-SITU EXPERIMENTAL DETERMINATION OF RESIDENT WATER SATURATION AND BRINE SALINITY IN A PETROLEUM RESERVOIR

Rice University

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IN-SITU EXPERIMENTAL DETERMINATION OF RESIDENT WATER SATURATION AND BRINE SALINITY IN A PETROLEUM RESERVOIR

by

Alan Douglas Mut

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

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MAY, 1982
ABSTRACT

In-Situ Experimental Determination of Resident Water Saturation and Brine Salinity In a Petroleum Reservoir

by

Alan Douglas Mut

A new technique has been developed to simultaneously determine the connate water saturation and the formation water salinity in a petroleum reservoir at connate water conditions. The technique involves the injection into the target formation of a known amount of some oleic material that has a salinity-dependent, limited ability to dissolve water. The formation oil will be miscibly displaced into the formation as water is extracted from the near-wellbore region. The well is then produced, and the effluent is analyzed to determine the water content.

Reversal of the flow does not lead to a reversible resaturation of the extracted region. Consequently, some water will be produced in solution in the oleic phase. Since the extraction and resaturation behaviors are both affected by the initial formation water salinity and saturation, the resulting production behavior can be used to indicate the initial salinity and saturation. This is done by matching the observed water production data to that predicted by a mathematical simulation of the experimental technique.

In this work, the theory is developed and compared with experimental results for a sandstone core.
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CHAPTER 1

INTRODUCTION

Knowledge of the relative fluid saturations existing in a petroleum bearing subterranean formation is essential for the proper and efficient exploitation of the oil reserve. Knowledge of the salinity of the formation water is essential to electric log interpretation, the most common method of estimating the distribution of fluid saturations. Both of these quantities are difficult to establish in reservoirs at connate water saturation conditions, since no free water phase can be produced. The objective of this study was to develop a method for determining both the resident water saturation and the water salinity in such a reservoir.

There are several methods currently available for determining the relative saturations of the reservoir fluids. Cores, when carefully obtained, provide actual samples of the reservoir and the fluids contained therein. If oil-base mud is used during the coring operation, both water saturation and formation water salinity can be determined by this method. However, the total sample volume is small with respect to the reservoir volume; unless extreme care is exercised, the sampling technique itself can contribute to changes in the amount and composition of the fluids present in the sample. Thus, the saturations determined by this method may not be representative of the saturations existing in the formation. The use of this method is also limited to new wells, or those wells which have not yet been drilled through the target formation.

Several logging techniques have been developed to obtain a detailed
description of the relative fluid saturations with respect to depth. In general, these methods measure the properties of the rock-fluid system as an entity. Many of these methods are dependent on an accurate determination of the formation porosity and other physical characteristics of the formation and its fluids. Most require that the formation water salinity be known a priori for a proper analysis of the resulting data to be made. The logging tools used display a rather shallow radius of investigation and, therefore, may be affected by the effects of borehole washout or drilling mud filtrate invasion. Recently, log-inject-log techniques have been developed to improve the ability to differentiate between the properties of the rock and its fluids. However, these methods must be carefully applied to avoid inducing changes in the near-wellbore fluid properties.

More recent work in the area of saturation determination involves the injection and production of trace materials into and out of the formation. A more common technique employed is the single-well chemical tracer technique developed by Deans and Shallenberger.\(^1\) Here, a reactive trace material is injected into the target formation. This material is then displaced further into the reservoir and allowed to react, thereby forming additional tracer materials. If the partitioning coefficients between the phases existing in the formation are different, for each trace component, chromatographic separation will occur as the fluids are produced back into the well. The saturation of the resident formation fluids can be determined by this separation. Unfortunately, it is generally necessary to have some knowledge of the formation brine salinity for the proper determination of the partitioning coefficients used in analyzing the data.

The method presented in this work is an extension of earlier work
by Deans and Bragg in which the saturation of an immobile gas phase was determined by means of an injection production extraction technique. The amount of gas present in the produced fluids was measured as a function of the volume of fluids produced back. The volume of gas-free water initially produced and the saturated gas solubility in the water are then used to calculate the residual gas saturation in the reservoir.

The method presented in this work can determine both the water saturation and the formation water salinity in a reservoir with an immobile aqueous phase. This technique involves the injection of an oleic material that has the ability to dissolve a limited amount of water. The solubility of water in the injected material is affected significantly by the presence of salt. During injection, the injected fluid displaces the oil phase while extracting water from the stationary aqueous phase near the wellbore. Continued injection leads to salt precipitation and, ultimately, the total disappearance of the aqueous phase near the wellbore. Reversal of the flow for production does not lead to a completely reversible resaturation of the extracted zone. The extraction and resaturation behaviors are both affected by the initial water saturation and brine salinity present. Thus, the resulting production behavior can be used to indicate the water saturation and salinity. An outline of the proposed method is as follows:

1) Inject a known volume of the oleic material into the formation which will both miscibly displace the oil phase and dissolve the water from the brine phase.

2) Produce the well while taking samples of the produced fluids, and analyze the samples for their water content.

3) Determine the connate water saturation and the salinity of the
brine by comparing the observed water production history to that predicted by a mathematical simulation of the experimental technique.
CHAPTER 2

MATHEMATICAL DESCRIPTION OF THE IN-SITU
EXTRACTION TECHNIQUE

Material Balance Equations Describing Multicomponent
Partitioning During Multiphase Flow

Adding an alcohol to an immiscible oil-brine system can cause the precipitation of salt. If a properly chosen alcohol is injected into an oil bearing porous medium containing an immobile brine, it will miscibly displace the oil phase while extracting water from the brine. Eventually, enough water will be extracted from the aqueous phase to cause the precipitation of a third phase. Due to the fractional flow constraints on the two-phase flow, reversing the direction of flow may not result in a detailed reversal of water transport among the phases. Consequently, the original saturation profile present in the porous medium may not be restored. The investigation of these flowing phase-behavior irreversibilities is the primary focus of this work.

A mathematical description of these effects of multicomponent multiphase partitioning requires a convective transport equation for each of the components in the system. The overall continuity equation for any non-reactive component "k" flowing in a porous medium is:

$$\frac{\partial}{\partial t} \left( \phi \left( \sum_{k=1}^{NP} \rho_{kp} S_p \right) \right) + \nabla \cdot \left( \nabla \cdot N_k \right) = 0$$

(1)

where

$$N_k = \sum_{p=1}^{NP} \rho_{kp} U_p + J_k$$

5
\( \vec{J}_k \) = the dispersive component of mass flux

\( \vec{U}_p \) = the local Darcy velocity of phase "p"

\( S_p \) = the local volume fraction of porespace occupied by phase "p"

\( \rho_{kp} \) = the local density of component "k" in phase "p" expressed with respect to the phase volume

\( N_P \) = the number of phases present

and \( \phi \) = the porosity of the porous medium.

Several assumptions and idealizations have been invoked to reduce equation (1) to a more tractable form:

1. The two-phase flow in the laboratory model described is one-dimensional and parallel. The model is homogeneous. The reduced flow equations are easily modified to describe one-dimensional radial flow near a wellbore of finite radius in a uniform porous stratum.

2. The phases are incompressible. Pressure has no effect on equilibrium behavior, fractional flow behavior, or any other dependent variable. The system is isothermal.

3. The partial mass volume of any component, \( \hat{v}_k \), is constant. The value is the same regardless of which phase the component occupies and is independent of composition.

4. The relative flow of the aqueous and oleic phases is governed by a fractional flow relationship which depends solely and uniquely on the aqueous phase saturation, such that

\[
\vec{U}_W = f_W \cdot \vec{U}
\]

and

\[
\vec{U}_O = (1-f_W) \cdot \vec{U}
\]
where \( U_p \) = the effective velocity of phase "p" in the matrix
\( U \) = the total Darcy velocity of the fluids in the matrix
\( f_w \) = the fractional flow relationship, dependent only on
the aqueous phase saturation \( S \).

(5) The phases are always and everywhere in local equilibrium.

(6) The aqueous phase can contain the three components - water, salt,
and alcohol. There is no oil in the aqueous phase.

(7) The oleic phase may contain three components - oil (which is treated
here as a single component), alcohol, and water. No salt is
present in the oleic phase.

(8) The salt phase is solid and contains only salt. This phase
does not flow, nor are salt crystals entrained by the fluid flow
in the porous medium.

(9) Dispersion is caused by hydrodynamic mixing and is therefore a
function of the overall composition of the flowing fluids. The
effects of molecular diffusion in the system are negligible.

In dealing with multiphase flow involving multicomponent partitioning
between the phases, it is convenient to distinguish between the overall
composition of the fluids in the porespace at a given time and the composi-
tion of the fluids flowing in the porespace. The overall volume fraction
of component "k" in the flowing fluids can be defined as the sum over all
phases of the products of the fractional flow of any phase "p" with the
volume fraction of that component in that phase.

\[
CF_k = \sum_{k=1}^{NP} f_p C_{kp} \quad \text{for } k=1,2,\ldots,NC
\]  

(2)

where \( CF_k \) = the overall volume fraction of component "k" in the flowing
fluids.
and \( C_{kp} = \rho_{kp} \hat{v}_{kp} \); the volume fraction of component "k" in phase "p".

Hereafter, \( CF_k \) will be referred to as the "flowing concentration of k".

The corresponding variable representing the overall volume fraction of component "k" present at any point in the porous medium, \( CP_k \), is defined in terms of the phase saturations and will hereafter be referred to as the "porespace concentration of k":

\[
CP_k = \sum_{k=1}^{NP} S_p C_{kp} \quad \text{for } k=1,2,...,NC \quad (3)
\]

As a consequence of the definitions of component volume fraction, fractional flow, and phase saturation, the following relations also hold:

\[
\sum_{k=1}^{NP} C_{kp} = 1 \quad \text{for } p=1,2,...,NP \quad (4)
\]

\[
\sum_{p=1}^{NP} f_p = 1 \quad \text{(5)}
\]

\[
\sum_{p=1}^{NP} S_p = 1 \quad \text{(6)}
\]

These relations may be used to show that the sum of the overall component volume fractions in either the flowing fluids, or the porespace itself, is unity.

\[
\sum_{k=1}^{NC} CF_k = 1 \quad (7)
\]

\[
\sum_{k=1}^{NC} CP_k = 1 \quad (8)
\]
The preceding assumptions and definitions can be utilized in rewriting equation (1) to obtain:

\[
\frac{\delta C_{P_k}}{\delta t} + U \frac{\delta C_{F_k}}{\delta x} = \delta \frac{\delta C_{F_k}}{\delta x} D \frac{\delta C_{F_k}}{\delta x} \tag{9}
\]

where \(D\) = the dispersion coefficient based on volume. The term on the right is present to describe the hydrodynamic mixing present in flow through porous media.

Many authors\(^3\) report that \(D\) is proportional to the fluid velocity at any point in the reservoir. Because of the assumption of incompressible linear flow, \(D\) can be taken to be constant and independent of position. Thus equation (9) can be reduced to the final form:

\[
\frac{\delta C_{P_k}}{\delta t} + U \frac{\delta C_{F_k}}{\delta x} = D \frac{\delta^2 C_{F_k}}{\delta x^2} \quad \text{for } k=1,2,\ldots,N_C \tag{10}
\]

By summing equation (10) over all components and using equations (7) and (8), it can be show that this set of equations is not linearly independent. The boundary value problem can be solved after reducing the system to \(NC-1\) independent equations, with the initial and boundary conditions dependent on the system under study.

**Solution of the Boundary Value Problem**

A central difference approximation for equation (10) can be obtained by using a Taylor's Series expansion and ignoring any third and higher order terms:

\[
\frac{\Delta C_{P_k}}{\Delta t_i} + \frac{1}{2} \frac{U}{\delta x} \left[ (C_{F_k})_{i+1} - (C_{F_k})_{i-1} \right] \equiv \frac{D/\phi}{(\Delta x)^2} \left[ (C_{F_k})_{i+1} - 2(C_{F_k})_i + (C_{F_k})_{i-1} \right] \tag{11}
\]
where the subscript "i" denotes the linear position in the matrix through the relation

\[ x = i \cdot \Delta x \quad \text{for } i = 1, 2, \ldots, NX \] (12)

where \( x \) = the linear distance from the point of injection

\( \Delta x \) = the length of each cell in the model (distance increment)

and \( NX \) = the number of cells in the model.

For convenience, the dependence of \( (CP_k)_i \) on \( (CF_k)_{i+1} \) can be removed by choosing the linear stepsize such that the following relationship is satisfied:

\[ D = \frac{1}{2} \frac{U}{\phi \Delta x} \] (13)

Then, equation (10) reduces to:

\[ \frac{\Delta CP_k}{\Delta t}_i \quad + \quad \frac{U}{\phi \Delta x} \left[ (CF_k)_i - (CF_k)_{i-1} \right] = 0 \] (14)

Aris and Admundson, Deans and other authors\(^4,5\) have noted previously that this equation describes a series of perfectly mixed stirred tanks, as shown in Figure 1. In such a system, the concentration of any tank in the series is independent of any tank concentration downstream. The advantages of this approach are twofold: First, the composition of each cell can be computed using an explicit finite difference equation dependent only on the compositions of the cell in question and that preceding it. Second, this choice of the distance increment reduces the equation to a first-order differential equation, resulting in a concomitant reduction in the number of necessary boundary conditions from two to one.
\begin{align*}
V \frac{\Delta \text{CP}_k}{\Delta t} &= Q \left[ (\text{CF}_k)_i - (\text{CF}_k)_{i-1} \right] \\
\end{align*}

where \( Q \) = the total volumetric flowrate \\
\( V \) = the total fluid volume in each tank \\
\( (\text{CP}_k)_i \) = the volume fraction of component "k" in tank "i" \\
\( (\text{CF}_k)_i \) = the volume fraction of component "k" in the fluids leaving tank "i"

FIGURE 1
The system under study in this work has four components; n-butyl alcohol, Arctic diesel, water, and sodium chloride, at 25°C and nominal pressure. Using the previously listed assumptions, the differential material balance equations for each of these components can now be rewritten explicitly as follows:

\[
\frac{\delta}{\delta t}[y_1(1-S-S)+x_1S]_i + \frac{U}{\psi\Delta x} ([y_1(1-f)+x_1f]_i - [y_1(1-f)+x_1f]_{i-1}) \equiv 0 \quad (15a)
\]

\[
\frac{\delta}{\delta t}[y_2(1-S-S)+x_2S]_i + \frac{U}{\psi\Delta x} ([y_2(1-f)+x_2f]_i - [y_2(1-f)+x_2f]_{i-1}) \equiv 0 \quad (15b)
\]

\[
\frac{\delta}{\delta t}[y_3(1-S)]_i + \frac{U}{\psi\Delta x} ([y_3(1-f)]_i - [y_3(1-f)]_{i-1}) \equiv 0 \quad (15c)
\]

\[
\frac{\delta}{\delta t}[x_4S + \overline{S}]_i + \frac{U}{\psi\Delta x} ([x_4f]_i - [x_4f]_{i-1}) \equiv 0 \quad (15d)
\]

where \( S \) = the aqueous phase saturation, the fraction of the porespace occupied by the aqueous phase

\( \overline{S} \) = the salt precipitate saturation, the fraction of the porespace occupied by salt precipitate

\( y_k \) = the volume fraction of component "k" in the oleic phase

\( x_k \) = the volume fraction of component "k" in the aqueous phase

\( f \) = the fractional flow of the aqueous phase

and the component subscripts 1, 2, 3 and 4 refer to n-butanol, water, Arctic diesel, and sodium chloride respectively.

As this is a four component system, only three of the equations listed above are linearly independent. In this work, the equation for n-butanol, equation (15a) was eliminated. As previously stated, the fractional flow depends only on the aqueous phase saturation and is, thus, a dependent
variable. In addition, the equilibrium relationships for this quaternary system along with equation (6) allow any component volume fraction within a phase to be expressed as a function of any two independent component phase volume fractions. To be complete, a theoretical model dealing with equations (15) above must be provided with fractional flow and equilibrium behavior.

In this study the equilibrium relationships are expressed as functions of the volume fraction of oil in the oleic phase, \( y_3 \), and the volume fraction of sodium chloride in the aqueous phase, \( x_4 \). These relationships are listed below:

\[
\begin{align*}
  y_1 &= 1 - y_2 - y_3 \\
  x_1 &= 1 - x_2 - x_4 \\
  y_2 &= y_2(y_3, x_4) \\
  x_2 &= x_2(y_3, x_4) \\
  y_4 &= 0 \\
  x_3 &= 0
\end{align*}
\]  

(16)

The actual functional relationships used for \( Y_2 \) and \( X_2 \) are reported in Appendix A. Figure 2 represents qualitatively the equilibrium behavior for this system at 25°C.

Fractional flow in the absence gravitational effects is given as

\[
f = \left[ 1 + \left( \frac{\mu_w}{\mu_o} \right) \frac{k_{ro}}{k_{rw}} \right]^{-1}
\]  

(17)

where \( k_{ro} \) = the relative permeability to the oleic phase

and \( k_{rw} \) = the relative permeability to the aqueous phase.

These functions are assumed to have the form

\[
\begin{align*}
  k_{rw} &= k_w'(S - S_{cw})^a \\
  k_{ro} &= k_o'((S_w)_{ro} - S)^b
\end{align*}
\]  

(17a)

where \( S_{cw} \) = the connate water saturation

\( (S_w)_{ro} \) = the saturation of water at residual oil saturation

and \( a, b, k_o' \) and \( k_w' \) are constants. \( \mu_w \) and \( \mu_o \) are the viscosities of the aqueous and oleic phases respectively, are assumed to be independent of composition.
QUATERNARY PHASE EQUILIBRIUM DIAGRAM
REPRESENTING THE QUALITATIVE BEHAVIOR
OF THE
OIL - BUTANOL - WATER - NaCl SYSTEM @ 25°C

FIGURE 2
S and $y_3$ are always dependent variables for this system of equations. Either $x_4$ or $\bar{S}$ is a dependent variable. If the two liquid phases are the only ones present, then $\bar{S}$ is by definition zero. However, if a salt precipitate has formed and both liquid phases are present, then the volume fraction of salt in the aqueous phase, $x_4$, attains its saturation value. In the latter instance, the salt phase saturation can be expressed by:

$$
\bar{S} = CP_4 - (x_4)_S S
$$

$$
x_4 = (x_4)_S
$$

where $(x_4)_S$ = the salt saturation limit of the aqueous phase. In this work, this limit is taken to be constant and independent of $y_3$.

When the aqueous phase saturation $S$ is zero, as is the case when the system is operating miscibly, equation (15) is no longer applicable. Instead, the more general equation (14) must be used. Here, the material balance is expressed in terms of the change in porespaces concentration as a function of the gradient of the flowing concentration at that point.

The miscible fluid is oleic in nature and is assumed to contain no salt. Consequently, any salt that is present must be in the solid salt phase and be stationary, since no mechanism exists for its transport. As such, the flowing concentration of any component other than salt in a miscible region is equal to the porespaces concentration of that component corrected for the salt precipitate saturation, $\bar{S}$.

$$
CF_k = \frac{CP_k}{1-CP_4}
$$

for $k=1,2,3$

$$
CF_4 = 0
$$

for $k=4$
Statement of the initial and boundary conditions completes the definition of this boundary value problem. The major purpose of this study was to develop a method of determining fluid saturations in reservoirs with an immobile aqueous phase. This phase was taken to have a constant saturation profile initially in the reservoir, consistent with the connate water saturation of the porous medium. This implies that the initial fractional flow of the aqueous phase at any point is zero. No alcohol is generally found in an undisturbed petroleum reservoir. Hence, the initial conditions at any point in the porous matrix are:

\[
\begin{align*}
CP_1(0,x) &= 0 \\
CP_2(0,x) &= S_{CW} (1-x_4^\circ) \\
CP_3(0,x) &= 1 - S_{CW} \\
CP_4(0,x) &= x_4^\circ S_{CW}
\end{align*}
\]

for \(0 < x < L\) \hspace{1cm} (20)

\[
\begin{align*}
CF_1(0,x) &= 0 \\
CF_2(0,x) &= 0 \\
CF_3(0,x) &= 1 \\
CF_4(0,x) &= 0
\end{align*}
\]

where \(x_4^\circ\) represents the original volume fraction of salt in the brine and \(L\) is the length of the linear porous medium under study.

As mentioned previously, only one boundary condition need be applied to the numerical approximation of these convective dispersion equations. However, the boundary conditions applied depend on whether injection or production is taking place. For the most part in this study, \(n\)-butanol was the only component introduced into the porous matrix by injection. Thus for injection, the boundary conditions are usually expressed as:

\[
\begin{align*}
CF_k(t,0) &= 1 \hspace{1cm} \text{for } k=1 \\
CF_k(t,0) &= 0 \hspace{1cm} \text{for } k=2,3,4
\end{align*}
\]

\(t > 0\) \hspace{1cm} (21)
If the reservoir is large with respect to the injected volume, the saturation and concentration profiles in regions far removed from the injection point should remain unaltered during injection. As a consequence, the only flowing component in these regions will be oil. The boundary conditions for production are then:

\[ CF_k(t, L) = 0 \quad \text{for } k=1,2,4 \quad t > t_{inj} \]  
\[ CF_k(t, L) = 1 \quad \text{for } k=3 \]

(22)

Simulation Model

A computer simulation program was developed to aid in the investigation of the irreversible flowing phase behaviors exhibited when flow is reversed in an alcohol-oil-water-salt system. The program uses the initial and boundary conditions given along with the equilibrium and fractional flow behavior supplied to calculate new values for the flowing concentrations and porosce concentration for each cell in the model. Each cell represents a finite volume increment of the linear porous medium being modeled. Cell concentrations can be calculated in sequential order from upstream to downstream due to the independence of the porosce concentration of any cell with respect to any cell composition downstream.

Specifically, the simulator program utilizes the following equation to solve for the new porosce concentration of each component in cell "i" at time "j":

\[ (CP_k)_{i,j} = (CP_k)_{i,j-1} + \tau[(CF_k)_{i} - (CF_k)_{i-1}j-1] \quad \text{for } k=2,3,4 \]

(23)

where \( \tau = \frac{U \Delta t}{4 \Delta x} \). The composition of the porosce is then checked to determine whether it lies within the miscible region. If the cell fluids
are miscible, equation (19) is used to calculate the new flowing compositions. The next cell composition is then calculated and the miscibility check is repeated. If the composition of a cell does not lie within the miscible region, further tests are performed to determine whether a salt precipitate is formed. A successive substitution routine is then utilized to solve for \( S, y_3 \), and either \( x_4 \) or \( S \) dependent on whether a salt phase is present. These values can then be used to calculate new values of the flowing concentrations according to the general definition, equation (2). Computation then proceeds on to the next cell. In general, the newly calculated flowing and porespace concentrations become the new set of initial conditions describing the concentration profiles in the porous medium, and the entire scheme is repeated at each new timestep.

The simulator program used in this work also has the capability of printing out the concentration profiles present in the model at any time, the porespace concentrations of any cell in the model as a function of time, and the flowing concentrations present in the last cell of the model as a function of time. The latter corresponds to the theoretically predicted production behavior. A general flowscheme of the simulation program is shown in Figure 3. The program listing and more detailed documentation are provided in Appendix C.

No-Dispersion Theory

The essential behavior of the system during injection can be explained by F.G. Helfferich's general theory describing multicomponent multiphase displacement in porous media. His theory is an extension of the Buckley-Leverett theory for incompressible flow of two immiscible phases. The extended theory describes the flow of an arbitrary number of phases with an arbitrary number of components partitioning
Input \( S \) and \( x_4^o \)

Set Initial Conditions
Equation (20)

Set Boundary Conditions
For Production
Equation (22)

Set Boundary Conditions
For Injection
Equation (21)

Begin Outer Time Loop
\( J = 1,2,\ldots,NT \)

Begin Inner Distance Loop
\( I = 1,2,\ldots,NX \)

Calculate the Component Material Balance
Equation (23)

Miscible ?

Yes

No

Salt Precipitate ?

Yes

No

Solve for \( S, y_3, \) and \( S \)

Solve for \( S, y_3, \) and \( x_4 \)

Calculate \( f \) and New Values for \( CF_k \)
Equations (17) & (2)

Calculate New Values for \( CF_k \)
Equation (19)

STOP after Production

FIGURE 3
between the phases. It requires as input fractional flow behavior and equilibrium data. His theory makes the same basic assumptions as are used in this work, with the additional constraint that there is no dispersion in the system. Hefferich's differential material balance for component "k" is:

$$\frac{\delta C_k}{\delta t} + \frac{U}{\phi} \frac{\delta C_k}{\delta x} = 0$$  \hspace{1cm} (24)

A property of exact differentials is used to show that the velocity of any porespace concentration of component "k" can be written:

$$V_{C_k} = \frac{\delta x}{\delta t} C_k = -\frac{(\delta C_k/\delta t)_x}{(\delta C_k/\delta x)_t}$$  \hspace{1cm} (25)

Equation (24) can be substituted into (25) to show that the velocity of any component concentration is proportional to the derivative of the concentration of that component in the flowing fluids with respect to its concentration in the porespace:

$$V_{C_k} = \frac{U}{\phi} \frac{\delta C_k}{\delta C_k} \bigg|_{dt=0} \quad \text{for } k=1,2,\ldots,NC$$  \hspace{1cm} (26)

In general, any arbitrary composition variation introduced into the system will not be propagationally stable, but will separate into several propagationally stable, or coherent, waves, each travelling at different speeds. The requirement for coherence is that all the component velocities at any point in time and space must have the same velocity:

$$\delta C_k = \lambda \delta C_k$$  \hspace{1cm} \text{for } k=1,2,\ldots,NC$$  \hspace{1cm} (27)

where \(\lambda\) has the same value for each component. Analogous equations can
be written for shock compositional variations. The total differentials of
the flowing component concentrations can be written as:

$$dC_{F_k} = \sum_{m=1}^{NC-1} \frac{\delta C_{F_k}}{\delta C_{P_m}} dC_{P_m}$$  \hspace{1cm} (28)

Taken together with the preceding equation, the coherence condition becomes:

$$\sum_{m=1}^{NC-1} \frac{\delta C_{F_k}}{\delta C_{P_m}} - \lambda dC_{P_k} = 0 \hspace{1cm} \text{for } k=1,2,...,NC-1$$  \hspace{1cm} (29)

This represents a typical eigenvalue system of order NC-1 whose character-
istic equation can be solved to obtain NC-1 eigenvalues, which in turn can
be used in equation (29) to find the corresponding eigenvectors. The eigenvectors represent the direction of the composition paths in the composition
space, and as such, they can be used to develop a path grid describing
the path of compositional variation of a point in space over time. Since
the sum over all components of the flowing component concentrations is
unity, any composition in a NC component system can exist in NC-1 dif-
ferent coherent waves, each having a different velocity. A composition
is characterized by the complete set of porespace component concentrations.

The series of curves in Figure 4 represent the path grid topology
for the ternary system diesel oil - water - n-butanol. Since NC = 3, any
composition in the two-phase region lies on the intersection of two paths,
each possessing different velocities. Accordingly, the paths have been
described alternately as "fast" and "slow" corresponding to the magnitude
of the eigenvalue associated with that path. In Figure 4, the "fast"
paths are marked by broken lines, whereas the solid lines denote the "slow"
paths. Several interesting features of the two-phase, three-component system
grid path topology are explained in Appendix B.
PATH GRID TOPOLOGY
for the
OIL - n-BuOH - H₂O SYSTEM @ 25°C

FIGURE 4
In the present case, n-butanol was injected into the formation at connate water saturation. This initial condition can be mapped as a point in the composition space lying on the line connecting the pure components oil and water. The injection of n-butanol into the matrix represents a single noncoherent compositional variation which, in this three component system, will split up into two coherent waves. The composition route of any point in the matrix will travel exclusively along the paths mentioned previously in the order of decreasing wave velocities. Thus the composition of a point in the porous medium will follow a "fast" path until that path intersects the "slow" path on which the injected composition lies. Figure 5a represents the composition route taken by any point near the injection point during injection. The resulting compositional behavior of the formation on inflow is shown in Figure 5b. This drawing represents the porespace concentration profile present in the reservoir at a given time. The bank of the injected alcohol pushes before it a growing alcohol-water equilibrium bank. The higher concentration of water in this zone represents the water extracted from the regions near the injection point. The length of this zone grows physically with time as a larger volume of water is extracted. The velocity of the transition zone between the equilibrium region and the unaltered regions of the reservoir is higher than that of the shock front separating the extracted region and the equilibrium zone. Hence, the "fast" path corresponds to the transition from the original conditions to the equilibrium point.

During the production phase of the push-pull extraction test the concentration paths are no longer easily predicted by Helfferich's method, because the initial condition present in the reservoir is now mapped by a curve in the composition space. However, one can logically
a. Composition route followed over time by a point in the extracted region during injection.

b. The resulting porespace concentration profile observed at the start of production.

FIGURE 5
deduce the behavior that will occur in a dispersion-free environment. The essentially plug flow behavior and the local equilibrium at all points at all times will cause an oleic phase consisting of butanol saturated with water to flow back into the extracted region of the formation. Since this fluid exists on the phase boundary, no aqueous phase is present. The extracted region is not resaturated, and consequently, water-saturated butanol is produced until the breakthrough of oil. This behavior is depicted in Figure 6. In this limiting dispersion-free case, the volume of water produced is equivalent to that originally held in the extracted zone as noted previously by Deans and Bragg. Thus the water saturation can be calculated as the ratio of the water produced to the total amount of fluids produced before any water production occurs. The latter represents the total volume of the extracted zone.

The Four Component System

The addition of sodium chloride to the oil-water-alcohol system complicates the behavior considerably. In general, increasing the number of components should increase the number of coherent waves caused by any noncoherent disturbance in the system, such as the injection of an alcohol into an oil-brine system. However, since salt is constrained to move only in solution in the aqueous phase, and since at connate water conditions the aqueous phase has little tendency to flow, the four component system displays only two composition variation waves, like the ternary system just discussed. In the absence of any salt movement, the porospace concentration of salt remains constant, so the system is forced to operate on a single plane in the three-dimensional composition space. However, the phase behavior is greatly affected by the sodium chloride concentration. The general behavior on inflow is much like that of the three-component system
a. i) Heavy line denotes locus of porespace compositions at beginning of production.
   ii) Heavy lines denote composition routes followed by points during production

b. Representation of resulting time dependent behavior of component porespace concentrations during production: i) beginning of production; ii) later; iii) later still; iv) final

c. Resulting water production behavior

FIGURE 6
just discussed. As the alcohol is injected, it extracts the water from the areas in the vicinity of the injection point and leaves behind a salt precipitate. As injection continues, an equilibrium flowing bank containing alcohol, and water is formed as more water is extracted from the injection region. It is this bank that displaces the oil further out into the reservoir. Figures 7, 8, and 9 show the composition route followed by a point near the point of injection and the resulting concentration profiles during injection.

The behavior during the production phase of the extraction process is sufficiently complex to warrant the use of a computer simulation. Nevertheless, the qualitative characteristics of the production behavior can still be described in terms of composition paths. Three basic types of production behavior were uncovered using computer simulation.

First, in the cases involving both higher connate water saturations and higher brine salinities, the concentration histories of the produced fluids were observed to have flat-topped peaks as shown in Figure 10a. Since the salinity depresses the amount of water the alcohol can absorb, the water peak arrival times decrease with initial brine salinity, because less water is extracted in the near injection point regions. Similarly, as the initial water phase saturation increases, the water peak of the production history arrives earlier due to the fact that a smaller volume of the formation had been extracted to a water-free condition. The peak concentration here represents the water content of butanol in contact with a salt saturated brine solution. As the oleic phase begins to flow back into the previously extracted region, it is of sufficient water content that contact with precipitated salt will cause the formation of an aqueous phase. Since the aqueous phase is immobile at low saturations, the water
FIGURE 7
OLEIC PHASE
COMPONENT VOLUME FRACTIONS

AQUEOUS PHASE
COMPONENT VOLUME FRACTIONS

- injected fluid (alcohol)
- oil
- water

Distance

Figure 8
OVERALL CONCENTRATION PROFILE ON INJECTION

\[ C_k = \sum c_{kj} S_j \]

where \( C_k \) = overall component volume fraction
\( c_{kj} \) = pure component volume fraction in phase "j"
\( S_j \) = saturation of phase "j"

FIGURE 9
a. Higher initial saturations and salinities

b. Lower salinities

c. Lower saturations

FIGURE 10
phase will serve to resaturate at least part of the extracted zone. However, since the entire zone is never completely resaturated due to irreversibilities in the flow behavior, the oleic effluent will be passing over zones containing a salt precipitate. Consequently, the water content of the effluent will never surpass that of butanol in contact with a saturated brine solution. Hence, a plateau effect is observed in the water production history.

The second production behavior pattern occurs at lower initial brine salinities, generally those less than 4.5 percent NaCl by weight. This behavior is shown in Figure 10b. The behavior in this case is dramatically different, because enough water is present in the oleic phase passing back into the extracted zone to resaturate the entire zone to the extent that no solid precipitate is left. As this occurs, the water content of the effluent can rise to whatever level would be in equilibrium with a brine of the concentration present at the outflow point in the formation. As the initial formation brine salinity approaches zero, the production behavior approaches that of the ternary oil - alcohol - water system. Figures 11 and 12 show the drastically different composition path behavior demonstrated in the high and low initial brine salinity cases respectively. Figure 13 shows the resulting concentration profiles left in the reservoir after production for both cases.

The third type of production behavior occurs in those cases where the initial water saturation is very low, generally for saturations less than 10 percent. This behavior stems from the higher level of dispersive mixing that occurs with the lower water phase saturations. The increased dispersion is a product of the decreased volume of injected alcohol invasion associated with a larger flowing phase saturation. In this case, the oil front
Composition Profile Present After Injection
- High Salinity Case -
10% NaCl brine (by weight)
\[ S_{CW} = 20\% \]

Composition Paths on a Plane of Constant NaCl Concentration Followed by Various Cells in the Finite Difference Model
Composition Profile Present After Injection
- Low Salinity Case -
2.5% NaCl brine (by weight)
\( S_{cw} = 20\% \)

Composition Paths on a Plane of Constant NaCl Concentration Followed by Various Cells in the Finite Difference Model During Production

FIGURE 12
Final H$_2$O Concentration Profiles

- Effect of Initial Brine Salinity

On Resaturation Behavior

FIGURE 13
reaches the production face of the formation before the water content of 
the produced fluids reaches its peak value. The presence of oil inhibits 
the ability of the oleic phase to hold water, and the water concentration 
drops off. Consequently, the plateau behavior is never realized. This 
type of behavior can also occur in formations with higher water saturations 
in the presence of high dispersion. A typical water production history 
for a low initial water saturation cases is represented by Figure 10c.
CHAPTER 3

EXPERIMENTAL DESIGN

Experimental Apparatus

The preliminary theoretical calculations showed that water could be extracted in a single well injection-production test. A laboratory experiment was then designed to generate a realistic set of data for comparison with the theoretical predictions.

The nature of the push-pull technique under study required that the experimental apparatus be designed so that the flow direction could be easily reversed and the volume of both the injected and produced fluids could be accurately monitored. If the results were to be meaningful, the experimental design had to conform as closely as possible to the assumptions used in the theoretical analysis. In order to satisfy the boundary conditions imposed here, the system was designed such that essentially pure alcohol was introduced at one end of an undisturbed linear system existing at connate water saturation conditions. During the production phase of the experiment, the oil which left the opposite end of the model during inflow was reinjected to reverse the flow. The latter condition corresponds to the situation present in a reservoir in which the fractional flow of oil is unity. The resulting experimental design employed to meet these requirements is depicted in Figure 14. A restored composite core consisting of seven Torpedo sandstone core plugs wrapped concentrically with Teflon tape and two rubber sleeves was mounted vertically in a triaxial core mounting tube. A simulated overburden force was applied to the composite core by filling the
Experimental Apparatus

300# Nitrogen Ballast for Core Pressure Maintenance

N₂

n-BuOH

3-way valve

Back-Pressure Regulator

Sample Collection Vial

600# Nitrogen Ballast for Sleeve Pressure Maintenance

N₂

Primol 355™

Core constrained in Triaxial Mount

Oil Reservoir

Sampling System

"Memory Loop"

Arctic Diesel

Pump Oil

Ruska Positive-Displacement Metering Pump

FIGURE 14
small annular volume between the mounting tube and the outer rubber core sleeve with a heavy oil under pressure. The overburden pressure was maintained at a relatively constant level inspite of temperature fluctuations by allowing the annular volume to communicate with a small ballast oil reservoir containing a sizeable nitrogen gas pocket. The rubber core sleeves prevented the heavy oil from entering the composite model.

On injection, the alcohol was introduced to the system by means of a one-liter capacity floating-piston transfer vessel. Pressure was maintained above the piston therein by nitrogen supplied from a large ballast tank. The pressure exerted by the nitrogen served to displace the piston, thus forcing the alcohol contained below the piston to flow through an appropriately adjusted three-way valve and into the top of the vertically mounted core. The resulting displacement of core fluids led to production from the opposite end of the core through a sampling system.

The sampling system was designed so that the fluids produced during the injection phase of the experiment could be tested to detect the presence of alcohol without the loss of system pressure. It consisted of two four-port Valco valves with adjacent entry and exit ports which were connected in a configuration that allowed a fixed-volume sample loop to be isolated from the flowstream. The isolated sample loop could be flushed and concurrently filled with diesel oil supplied from a repeating spring-return pipette syringe at atmospheric pressure while the pressurized fluids flowing from the core bypassed the sampling system. The sample-flushing syringe was refilled by gravity drainage from another small oil reserve. Because all of the fluids involved were
relatively incompressible, no appreciable change in system pressure took place when the sample loop was returned to the flow-stream.

Once past the sampling system, the produced fluids passed through a fifty foot section of 1/8-inch ID copper tubing with a total internal volume of 32.6 cc. This so-called "memory loop" was installed in order to preserve the history of any alcohol or water-containing fluids that may accidentally have been pushed beyond the confines of the composite core. Thus, should any composition variations emerge from the model during injection, the fluids would return during production in the same relative order in which they left. Fluids flowed from the memory loop into a second floating-piston transfer vessel containing oil above the piston with pump oil below it. The pump oil was consequently displaced into a 500 cc capacity Ruska volumetric piston displacement pump whose piston withdrew at a constant rate. As the fluids in the system, with the exception of nitrogen, were relatively incompressible, it was essentially the Ruska pump that controlled the volumetric flowrates in the system. The Ruska pump was used to indicate the total volumes of fluid displaced.

For production, the piston movement of the Ruska pump was reversed and the three-way valve on the now downstream end of the core was adjusted so that the fluids would flow through a back pressure regulator whose diaphram pressure was maintained by the previously mentioned nitrogen ballast tank. From this point the produced fluids dripped into graduated vials held in a "Fractomat" automatic sampling system which has the capability to change collection vials at preset intervals of time. In this fashion, the entire production history of the push-pull extraction was preserved.
EXPERIMENTAL PROCEDURE

A. Preliminary Preparation

The composite core model used in this confirmation experiment consisted of seven 1.5-inch diameter plugs of Torpedo sandstone with a total length of 94.23 cm. Torpedo was chosen because of its reputation for homogeneity and the fact that it generally displays good porosities along with relatively high permeabilities. The core was believed to be totally saturated with Arctic Diesel, but preliminary tracer experiments showed that it had an apparent 0.9 percent water phase saturation. The core was subsequently flooded with a 5.0 weight percent sodium chloride brine to establish a more significant water saturation. During this process, some 206.8 cc of Arctic diesel were displaced from the core model indicating that an equivalent amount of the injected brine had been captured by the model. The core was then "restored" to a near connate water condition by flooding with approximately eight pore volumes of Arctic diesel. 148.6 cc of brine were displaced during the restoration process in which the last observed fractional flow of water was on the order of 0.25 percent.

Two separate tracer tests, each utilizing two tracer components displaying different equilibrium concentration ratios with respect to the oil and water phases, were performed in an effort to confirm the prior volumetric measurements and to determine the composite model's pore volume and aqueous saturation. The pore volume of the model was determined to be approximately 270 cc indicating a porosity of 25 percent. The apparent aqueous phase saturation was 22.4 percent. More explicit details regarding the preparatory experimental work can be found in Appendix D.

B. Confirmation Experiment

After the core had been successfully restored, the valves on either
end of the core were closed so that the existing fluid saturations would not be altered. At this time, the apparatus described earlier was constructed. The first floating-piston transfer vessel and all appropriate lines - those upstream from the core during injection and those downstream from the core during production - were filled with what was later found to be 0.61 volume percent water contaminated n-butanol. The sampling system, memory loop, the space above the piston in the second transfer vessel and all associated lines were filled with Arctic diesel. In such fashion, both the injection and production period boundary conditions could be met. The core was then pressurized at 270 psig using the Ruska pump. Sleeve pressure was maintained at 710 psig. The Ruska pump was then reversed and the core was opened to flow at approximately 8.3 cc/hr. This relatively slow rate, which corresponds to a linear velocity in the core of 2.3 ft/day, was selected so that the contact time would be sufficient for local equilibrium to be approached. The produced fluids were sampled occasionally to detect the presence of butanol. Trace levels of the alcohol were discovered after 194 cc of injection but the flow was allowed to continue to 200 cc total injected fluid as a matter of convenience. At this time, the flow was reversed and the three-way valve on the injection end of the core was adjusted so that the produced fluids flowed through the back pressure regulator into the collecting vials. A total of 400 cc was produced.

Production sample collection vials were changed at fifteen minute intervals. The samples obtained were analyzed to determine their water content by means of the Karl Fisher method \(^8\) "Dead-Stop" titration technique. Here, the Karl Fisher reagent, consisting of pyridine, iodine, sulphur dioxide, and methanol, reacts stoichiometrically with water. The endpoint
is marked by the dramatic decrease in the electrical resistance of the titration solution caused by any excess of the reagent. Tabulated values for the water content of the samples are presented in Table 1.

Following the confirmation experiment, the composite core was disassembled into its component core plug sections. The core plugs were then extracted by the Dean Stark method using boiling toluene to extract water from the cores. The salt precipitate remaining in the cores was extracted by steam condensation. The saline solutions resulting from the latter extractions were analyzed by titration with a silver nitrate solution to determine the amount of salt extracted. Table 2 shows the amounts of water and salt that were extracted from each core plug. Note that the first plug was divided in two prior to the extraction processes in order to provide a more detailed analysis of the saturation profile left as a result of the confirmation experiment.
<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>SAMPLE VOLUME</th>
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<th>VOL. PERCENT WATER</th>
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**SUMMARY OF KARL FISCHER ANALYSES OF PRODUCTION SAMPLES**

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* The original brine concentration was 52.6 mg NaCl/ cc H₂O
Chapter 4

RESULTS

Theoretical Prediction

As explained in Chapter 2, when a suitably chosen alcohol is injected into a porous medium originally at connate water saturation conditions, the alcohol displaces the oil phase and extracts water from the aqueous phase, causing salt to precipitate. At the end of injection, the porous formation near the point of injection is totally extracted, containing only precipitated salt in the presence of the injected alcohol. When the flow direction is reversed, the water-saturated oleic phase flows back through this extracted zone, partially resaturating it. However, since an alcohol containing water can exist in equilibrium with a salt-saturated brine, some water can actually be extracted from the porous medium. Consequently, since the aqueous phase present in the reservoir is not mobile, the extracted zone will not become fully resaturated. This irreversibility is the basis for measuring water phase saturation and salt concentration in an oil reservoir.

The theory presented in this work predicts that over the higher ranges of initial brine salinity, the water content of the produced fluids as a function of time can be represented by a flat-topped peak. This plateau behavior results from the fact that the zones very near the injection point never reabsorb water beyond the point of salt saturation. The salt precipitated during the injection period is not completely redissolved. As a result, the fluids flowing through this region must be in equilibrium with a salt-saturated aqueous phase and
salt precipitate. The maximum water concentration thus observed is equivalent to that of an oil-free alcohol phase in contact with a salt saturated brine.

The presence of salt significantly decreases the ability of an alcohol to absorb water. Thus as the original brine salinity increases for any given original water phase saturation, a given amount of injected alcohol will extract the water from a smaller volume of the porous matrix. Consequently, the arrival time of the water-bearing alcohol will be shorter during production in a reservoir with a higher initial salinity. This effect of salinity on production behavior is shown in Figure 15 for the Arctic diesel - n-butanol - water - sodium chloride system studied in this work. Similarly, for a given level of original brine salinity, any volume of injected alcohol will extract a proportional volume of water. Consequently, a smaller volume of the reservoir will be extracted at higher original aqueous phase saturations. As such, the dimensionless arrival time of the water in the produced fluids will also be shorter for higher saturations. The effects of original aqueous phase saturation on the production behavior are illustrated in Figure 16. The arrival time of the oil front is very nearly independent of saturation and salinity effects and is directly related to the volume of the injected fluids. Thus, the amount of water extracted increases with both increasing salinity and increasing water saturations in the case of higher original brine salinities.

The production behavior deviates from that described above over the lower ranges of original brine salinity. In this case, the entire extracted region eventually becomes resaturated to the extent that no salt precipitate is present. The plateau behavior of the high salinity
Effect of Initial Brine Salinity on Production Behavior

\[ S_{CW} = 20\% \]

5% NaCl brine (by weight)

FIGURE 15
Effect of Initial Water Saturation on Production Behavior
10% NaCl brine

$S_{cw} = 30\%$

10%

20%

Percent $H_2O$ by Volume

volume produced

volume injected

FIGURE 16
cases is exhibited while the extracted zone is resaturated. At the point where the last bit of precipitate is redissolved, the water content of the oleic phase is no longer constrained to the "salt-saturated" value. As the resaturation process continues, the salinity of the aqueous phase drops, and higher concentrations of water can then appear in the produced fluids until oil breakthrough appears. Thus, a "hump" will be observed on the trailing end of the water peak of the production history. The point of deviation from the plateau behavior marks the point at which the last of the precipitate is redissolved. The effects of brine salinity and water saturation on the water production behavior in instances of low initial brine salinity are depicted in Figures 17 and 18 respectively. Original brine salinity and water saturation both affect the arrival time of the water-containing alcohol much as they did in the higher salinity cases. That is, the arrival time decreases with both increasing saturation and increasing salinity. The effects of saturation and salinity on the dimensionless arrival time are depicted in Figure 19.

Although the behavior of the peak arrival time in the low salinity case is quite the same as that in the high-salinity cases, the behavior with respect to the volume of water extracted is quite different in the low-salinity case. Due to the increased ability of the produced fluids to hold water as the salinities in the resaturated zone drop, a substantially greater volume of water can be extracted in the lower salinity case. The previously described deviation from the plateau behavior occurs earlier, and higher maximum water concentrations are observed during production as the original salinity decreases. This effect overwhelms the effect of the later arrival time associated with decreasing salinity on the
Effect of Brine Salinity on Water Production History

- Low Salinity Case -

\[ S_{cw} = 30\% \]

![Graph showing the effect of brine salinity on water production history. The graph illustrates various salinity cases with labeled percentages (1%, 2%, 3%, 4%) and shows the volume produced relative to the volume injected. The figure is titled "FIGURE 17".](image-url)
Effect of Initial Water Saturation on Water Production History

- Low Salinity Case -
2.5% NaCl brine

FIGURE 18
extracted volume of water. Thus, in the instance of low initial brine salinity, the volume of extracted water increases as salinity decreases whereas at high salinities, the opposite is true. (See Figure 20.) This indicates that the dimensionless amount of water produced will pass through a minimum at some value of initial brine salinity for any given initial water saturation. For the Arctic diesel - n-butanol - water - salt system studied here, this minimum occurs approximately at the salinity corresponding to a 4.5 percent by weigh NaCl brine, and it seems to be relatively independent of initial saturations. For initial brine salinities lower than 4.5 percent, the arrival time and the volume of water can be used to determine the original water saturation and brine salinity uniquely. Parametric curves representing this relationship are depicted in Figure 21.

The other parameters affecting the water production behavior are the fractional flow behavior and the dispersion. All the Figures previously referred to in this section represented behavior that would occur with a fixed level of dispersion in the absence of any appreciable water phase flow. Dispersion does not affect the behavior qualitatively except in that it creates a smearing of the production history. The effect of dispersion on the production history can be seen in Figure 22. The arrival time of the extracted water is obviously affected by the dispersive mixing, but the volume of water extracted is relatively insensitive to the level of dispersion.

When the aqueous phase is mobile to any significant degree, the injected alcohol displaces the oil in the formation and also the aqueous phase to some limited extent. Thus water transport is caused both by extraction of the near-injection point region by the injected alcohol
Effects of Initial Brine Salinity and Water Saturation on the Volume of Water Extracted

Volume of $H_2O$ produced/volume alcohol injected

Percent NaCl by weight in original brine

FIGURE 20
Effect of Dispersion on Water Production History

$S_{cw} = 22\%$

2.5% NaCl brine

FIGURE 22
Effect of Aqueous Phase Fractional Flow on the Water Production History

\[ k_{ro} = ((S_w)_{ro} - S)^{BO} \]
\[ k_{rw} = (S - S_{cw})^{AW} \]
\[ \nu_w / \nu_0 = 1.0 \]

\( S_{cw} = 0.20 \)
\( (S_w)_{ro} = 0.70 \)
\( BO = 3.0 \)

FIGURE 23
and by aqueous phase flow. The overall effect is to create a larger extracted region and consequently the arrival time of the leading edge of the peak is slightly longer. The arrival time of the trailing peak is slightly shorter because some of the water initially present is displaced in front of the alcohol-brine equilibrium bank, thus creating an effectively smaller zone of alcohol invasion. (See Figure 23)

Experimental Results

Production samples from the confirmation experiment were analyzed by means of the Karl Fischer titration technique to determine water content. The results of this analysis are shown graphically in Figure 24. Tabulated values of this data can be found in Chapter 3. This data shows the flat-topped behavior expected, but it also shows a definite indication of the "bump" phenomenon described earlier. Deviation from the plateau behavior was not expected in this case where the core originally contained a 5.0 percent by weight sodium chloride brine. The theory predicts such behavior only for those cases with initial salinities of 4.5 percent or less. The appearance of this bump is, however, readily explained by considering the mechanism of salt transport.

The theoretical model assumed that no salt was present in the oleic phase or in any miscible fluid. As such, the only mechanism available for salt transport is that of aqueous phase flow. If the fractional flow of water is small, then little salt movement should take place, and a porous stratum with an initially uniform saturation profile should be left with a constant amount of salt throughout. Figure 25 shows that the assumed salt transport mechanism is incorrect. This illustration represents the amount of salt remaining in each plug of the composite core following the confirmation experiment. Clearly, a considerable amount of salt has been
Results of the Karl Fischer Analyses of the Produced Fluids

Percent $H_2O$ by Volume

Cubic Centimeters of Fluid Produced

FIGURE 24
stripped from the first two core plugs. Later experiments have shown that while the salt concentration present in the oleic phase in contact with a salt-saturated aqueous phase is small, it cannot be neglected when large volumes of fluid are concerned. Apparently, as the water-containing oleic phase flows back over the extracted zone, it absorbs small quantities of salt. When large volumes of this water-containing oleic fluid flow through this region, a significant salt stripping effect results. This lowers the apparent "salinity" of the extracted region causing resaturation behavior similar to that of a low initial brine salinity case. Hence, a hump is observed.

The amount of salt remaining in the first core plug corresponds roughly to that which would be left in the case of an initial 3.5 weight percent sodium chloride brine should no salt transport occur. The composite model itself was determined to have an initial aqueous phase saturation of 22.1 percent. The theoretically predicted production behavior for a case with a 22 percent connate water saturation with a 3.5 percent sodium chloride brine is compared to the actual production behavior observed in Figure 26. The plot of the experimental data has much the same shape as that of the theoretical curve. The background water content of the early production times is indicative of the fact that water contaminated n-butanol was injected into the composite core.

Although the similarity of the experimental production history to predicted production behavior adds some credence to the theory presented in this work, the experiment and theory are not in good quantitative agreement. The arrival time of the water production is later than was predicted and the water content of the produced fluids was lower than the expected value.
Comparison Between Experimental Results and Theoretical Predictions

Percent H$_2$O by Volume

Cubic Centimeters of Fluid Produced

Theory
Observed Data

FIGURE 26
An uneven initial saturation profile is most likely one cause of the discrepancy between the observed and the predicted arrival times of the water-containing fluids. Figure 27 shows the comparison of the observed and predicted amounts of water left in the core after the production phase of the test. The larger extracted volume observed is consistent with the later arrival time with respect to the theoretical prediction. This figure also shows that the volumes of water remaining in the four core plugs farthest from the injection point were greater than the predicted values based on a constant initial saturation profile. In the absence of aqueous phase flow, this accumulation of water would indicate that the initial saturation profile was not flat. The original saturation of the cores on the injection end of the composite model appears to have been below the average model saturation. As a consequence, a larger volume would be extracted, and the arrival time of the water production would be delayed.

Significant fractional flow of the aqueous phase, as mentioned in Chapter 2, can also cause a delayed arrival time. However, there was no evidence of any free water phase in the samples taken during the injection period. In addition, no water was found in the second transfer vessel. Had any water been produced as a free phase during injection, it would have accumulated at the bottom of this vessel.

Data collected during the preliminary experimental work indicated that approximately 61 cc of 5.0 weight percent NaCl brine were present in the core initially for the confirmation experiment. This corresponds to 60 cc of pure component water. A total of 5.8 cc water was extracted during the push-pull extraction experiment as determined by integration of the experimental production data. An additional 49.3 cc was recovered
Comparison Between Experimental Results and Theoretical Predictions

predicted values for water remaining based on $S_{cw} = 22\%$, 3.5\% brine

FIGURE 27
upon extraction by the Dean Stark technique. Thus, roughly eight percent of the water remains unaccounted for. The apparent salt concentrations present in the four core plugs farthest from the injection end of the model are close to the concentration of the brine originally injected into the composite core model, as shown in Figure 28. Furthermore, these concentrations show the expected monotonic increase with increased distance from the point of injection. This behavior was predicted by the theoretical model and is caused by a slight variation in the aqueous phase saturation left in the water-alcohol equilibrium regions after the production period. The mathematical model, of course, assumes that no salt movement occurs in the absence of aqueous phase flow. In reality, this monotonic trend could be partially due to the salt stripping effect of the flowing fluids. Regardless, this information indicates that the Dean Stark extractions were fairly complete, at least for the four core plugs discussed here. The possibility does exist, then, that the original water saturations present in the core were lower than the preliminary experiments indicated. This also could explain the discrepancy between the experimentally observed and the theoretically predicted water production arrival times.

As mentioned earlier, the height of the water production history plateau was lower than expected. The theory predicted that the produced fluids would be in equilibrium with a salt-saturated aqueous phase, and as such, should exhibit a water content by volume of 6.08 percent during the plateau production period. The observed water content of the produced fluids during this period was approximately 5.25 percent by volume. This lower water content could be caused by a change in equilibrium behavior resulting from contact with the various matrix
cementing materials or from ions introduced into the fluid system by ion exchange with the clay materials present in the matrix. Similar behavior would be expected if the injected fluid was contaminated with oil or if bypassing occurred. However, no evidence was found to substantiate either of these explanations.

Some of the discrepancy between the theory and the observed behavior is due to the flawed equilibrium model used in the theoretical work. Not only does this model not account for the fact that the oleic phase can hold salt, but recent experiments have shown that the equilibrium data used to construct the model was in error. The saturation limit of water in salt-free n-butanol is actually about 17.6 percent by volume, whereas the mathematical eqilibrium model was based on data indicating that this saturation limit was only 16.3 percent. A higher saturation limit at any given salt concentration would cause a larger volume of water to be extracted, and again, the water production arrival time would be delayed.

Finally, it is important to note that since fluids will generally flow along the paths of least resistance, the technique developed in this work will tend to indicate permeability weighted saturations in a real, nonhomogeneous reservoir. As a consequence, the effective saturation indicated by such an experiment will not necessarily coincide with the volume average formation fluid saturation.
CHAPTER 5

CONCLUSIONS

Summary

As stated in the introduction, the goal of this work was to develop an in-situ experimental technique for determining both the water phase saturation and the brine salinity present in a petroleum reservoir at connate water saturation conditions. This objective was met with partial success with the development of an injection-production extraction technique involving an injected fluid with a salt concentration dependent, limited capability to hold water. Experimental production history was compared to behavior predicted by mathematical modeling of the experimental system. Results of theoretical modeling of the technique developed indicate that both the saturation and salinity can be determined uniquely over some ranges of initial brine salinity.

For the Arctic diesel - n-butanol - water - sodium chloride system studied in this work the results of the theoretical simulation can be stated simply as follows: At higher resident brine salinities, a plot of the water production history will show a flat-topped peak. The expected arrival time of this peak is shorter as either the initial saturation or salinity is increased. The peak water content and the trailing edge of the water production are not affected by either of these variables. As such, the saturation and salinity demonstrate an additive effect that cannot be separated to determine either variable uniquely. At resident brine salinities less than 4.5 percent sodium chloride by weight,
production behavior deviates from the plateau behavior of the higher initial salinity cases. The peak height observed increases dramatically as the original brine salinity decreases. In this instance, arrival time is a good indication of saturation while the volume of water extracted rises with either increased saturation or decreased salinity. The arrival time and extracted volume can be used to determine both quantities over the lower ranges of initial brine salinity.

The existing experimental evidence is generally supportive of the theory presented in this work. This evidence does, however, indicate that the simplifying assumption that salt only exists in solution in the aqueous phase or as a precipitate is not valid. The evidence also suggests the need for additional research concerning the effect of multiple component salt systems and of formation materials on the equilibrium behavior. Additional study should be directed toward the use of different injection materials. Preliminary theoretical work indicates that the range of initial salinities over which the so called bump phenomenon occurs can be increased by choosing an injection fluid whose salt-saturated water saturation limit is smaller. An example of such a fluid is diesel oil-contaminated alcohol. The sensitivity of the production behavior to salinity increases as the salt-free saturation limit of water in the injected fluid is increased.

Clearly, obtaining meaningful results by this method requires that accurate equilibrium data be determined at reservoir conditions. Such data may be difficult to obtain in practice. This problem can be circumvented by initially displacing the existing oil phase in the reservoir with some oleic fluid for which the equilibrium properties are well known.
or easily determined. The latter technique would be especially useful in those reservoirs whose oils display excessively wide boiling point ranges such that the oil cannot be effectively treated as a single component.

As related in the introduction, should this method be developed to the point of commercial application, it will present several distinct advantages over the currently available methods for determining fluid saturations in a petroleum reservoir. This method can measure the salinity of the formation brine in certain instances. Interpretation of most other methods requires that the salinity is known a priori. If the brine salinity is known, the saturation can be determined in all instances. Also, in addition to the advantage it shares with the single-well tracer technique, a large volume of investigation, the method presented in this work does not require any reaction period, and consequently, interpretation of the results will not be complicated to the same degree by fluid drift in the formation. Additionally, the theory predicts that, barring large dispersion effects, the production volume necessary to observe the final water produced is nearly independent of saturation or salinity effects. This volume is slightly larger than the injected volume. As a result, the field effort associated with this method should not only be shorter, but should also be more easily predicted.

As discussed previously, the technique presented here cannot determine the saturation and salinity of the resident aqueous phase uniquely for those cases with high initial brine salinities. In such cases, these variables only affect the arrival time of the water production in an additive fashion. Some potential exists for the development of a double injection-production extraction technique in which two different injection
fluids displaying different water solubility limits would be used. The production behavior from the two tests would provide two separate additive relations which could be used to solve for both variables uniquely.
APPENDICES
APPENDIX A

The Phase Equilibrium Model

The mathematical model representing the four component equilibrium system studied in this work — the Arctic diesel - n-butanol - water - sodium chloride system at 25°C and nominal pressure — was based on the knowledge of the equilibrium behavior of two three-component systems: the oil - alcohol - water system and the alcohol - water - salt system. The oil - water - salt system was taken to be completely immiscible.

The phase behavior of either system was determined using the Karl Fischer aquametry technique to determine the water content of the oleic phase and chromatographic analysis to determine the amount of n-butanol in the aqueous phase. The salt was assumed to remain in the aqueous phase. This data and the mass balance relationships provided enough information to completely solve for the equilibrium tie-line relationships.

Data for the oil - n-butanol - water system at 25°C is shown in Figure A.1. Functional relationships were developed to approximate this phase behavior in the absence of salt:

\[ y_1(y_3) = 1 - y_2 - y_3 \]
\[ y_2(y_3) = 0.163 \exp(-3.0y_3) - 0.008115(y_3)^2 \]
\[ x_1(y_3) = 0.092 - 0.02647 y_3 - 0.06553(y_3)^{12} \]  \hspace{1cm} (A-1)
\[ x_2(y_3) = 1 - x_1 \]
\[ x_3(y_3) = 0 \]

The functional relationships for \( x_1 \) and \( y_2 \) are plotted against the experimental data in Figures A.2 and A.3.

Phase equilibrium data for the n-butanol - water - sodium chloride
system is shown in Figure A.4. The functional relationships developed
to approximate this behavior are as follows:

\[
\begin{align*}
y_1(x_4) &= 1 - y_2 \\
y_2(x_4) &= 0.163 \exp(10.67 \times 4) \\
x_1(x_4) &= 0.092 - 0.16(x_4^{0.333}) \quad \text{for } x_4 < 0.018 \\
&= 0.050 - 0.5155(x_4 - 0.018) \quad \text{for } x_4 > 0.018 \\
x_2(x_4) &= 1 - x_2 - x_4
\end{align*}
\] (A-2)

These functions represent the behavior of the four component system in
the absence of oil. The functional approximations to \(x_1(x_4)\) and \(y_2(x_4)\)
are represented in Figures A.5 and A.6.

The assumption was made that the effects of \(y_3\) and \(x_4\) on the concent-
ration of water in the oil phase were independent of one another. That is,
the quality of the relationship between \(y_2\) and \(y_3\) in a salt-free system
is maintained, but the absolute magnitude is adjusted corresponding to
the aqueous phase salt concentration present. The resulting relationship
representing the volume fraction of water in the oleic phase of the four-
component system is:

\[
Y_2(y_3, x_4) = \left[ y_2(x_4) \cdot y_2(y_3) \right] / 0.163
\] (A-3)

A similar assumption was made regarding the effects of \(y_3\) and \(x_4\) on the
concentration of alcohol in the aqueous phase resulting in:

\[
X_1(y_3, x_4) = \left[ x_1(x_4) \cdot x_1(y_3) \right] / 0.092
\] (A-4)

Mass balance relations provide the relationships for \(x_2(y_3, x_4)\) and \(y_1(y_3, x_4)\).

\[
\begin{align*}
x_2(y_3, x_4) &= 1 - X_1(y_3, x_4) - x_4 \\
y_1(y_3, x_4) &= 1 - Y_2(y_3, x_4) - y_3
\end{align*}
\] (A-5)
Phase Equilibrium Data
for the
Oil - n-BuOH - H₂O System @ 25°C

Arctic Diesel

H₂O

0.092 volume fraction n-BuOH

0.163 volume fraction H₂O

n-BuOH

FIGURE A.1
\[ x_1(y_3, x_4=0) = 0.092 - 0.02647y_3 - 0.06553(y_3)^{12} \]

- experimental data

**FIGURE A.2**
\[ y_2(y_3, x_4=0) = 0.163 \exp(-3.0y_3) - 0.00812(y_3)^2 \]

FIGURE A.3

<table>
<thead>
<tr>
<th>Volume fraction H_2O in oleic phase (y_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Volume fraction H_2O in oleic phase (y_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
</tr>
</tbody>
</table>

experimental data

\( x_2 \)
Phase Equilibrium Data
for the
n-BuOH - H₂O - NaCl System @ 25°C

 salt precipitates below this line

FIGURE A.4
$x_1(y_3=0,x_4) = 0.092 - 0.16(x_4)^{3.33}$  \[ x_4 < 0.018 \]

$= 0.050 - 0.5155(x_4-0.018)$  \[ x_4 > 0.018 \]

experimental data

saturation limit

FIGURE A.5
n-BuOH - H₂O - NaCl System (No oil present)

\[ y_2(y_3=0,x_4) = 0.163 \exp(-10.67x_4) \]

- experimental data

**FIGURE A.6**
APPENDIX B

Path Grid Topology For 3-Component, 2-Phase System with S-Shaped Fractured Flow Curves

(1) Any single phase region contains no paths, because all points contained therein satisfy the coherence condition.

(2) Each tie-line is a path.

(3) The equivelocity curve is a path.

(4) The envelope of the two phase region is a path.

(5) Each tie-line has two singular points at which two paths are tangential. Each tie-line is a "fast" path between these singular points and a "slow" path between the points and the phase envelope.

This type of topology was discovered by George Hirasake in 1977 by numerical computation. The behavior can be proven easily analytically and is explained in more detail in Reference 6. This information was included only to give the reader a slightly better qualitative understanding of the topology of the system in question.
APPENDIX C

Detailed Logic Diagram of the Numerical Simulation Model
INPUT: $S^o, x_4^o, (x_4)_5^o, \varepsilon, NC, NT, NX$

fractional flow equation (FRACFL)
equilibrium behavior model (COMPS)

SET INITIAL CONDITIONS

\[
\begin{align*}
(CP_2)_i &= (1-x_4) S^o \\
(CP_3)_i &= 1 - S^o \\
(CP_4)_i &= x_4 S^o \\
(CF_2)_i &= (1-x_4) f \\
(CF_3)_i &= 1 - f \\
(CF_4)_i &= x_4 f \\
STOS2_i &= S^o
\end{align*}
\]

BEGIN OUTER TIME LOOP

\[
j = 1, 2, 3, \ldots, NT
\]

SET BOUNDARY CONDITIONS

\[
k = 2, 3, \ldots, NC
\]

\[
CSTO_k = 0
\]

production ?

\[
CSTO_3 = 1
\]

BEGIN INNER DISTANCE LOOP

\[
\begin{align*}
(i) &= 1, 2, 3, \ldots, NX \\
LAST_i &= i
\end{align*}
\]

CALCULATE COMPONENT MATERIAL BALANCE

\[
\begin{align*}
(CP_k)_i &= (CP_k)_i + \tau [ CSTO_k - (CF_k)_i ] \\
CSTO_k &= (CF_k)_i
\end{align*}
\]

CALCULATE MISCELLIBILITY CRITERION

\[
\begin{align*}
y_3^* &= (CP_3)_i / (1-CP_4)_i \\
WATEST &= (1-CP_4)_i y_2(y_3^*, (x_4)_{sat})
\end{align*}
\]
CHECK FOR MISCIBILITY

\((CP_2)_{i+1} \geq \text{WATEST}\)

YES; IMMISCIBLE

NO; MISCIBLE

\((CF_2)_{i+1} = (CP_2)_{i+1}\)

\((CF_3)_{i+1} = (CP_3)_{i+1}\)

\((CF_4)_{i+1} = 0\)

\(S_{\text{STOS2}} = 0\)

\(S = S_2\)

\(x_4 = CP_4/S\)

\(\bar{S} = 0\)

\(x_4 < (x_4)_s\) \(\Rightarrow\) 2 phases

\(x_4 = (x_4)_s\)

\(\bar{S} = CP_4 - (x_4)_s \cdot S\)

\(y_3 = (CP_3)_i / (1 - S - \bar{S})\)

call COMPS to calculate \(y_2\) and \(x_2\)

\(S_2 = \frac{(CP_2)_{i+1} - (1 - \bar{S})y_2}{x_2 - y_2}\)

COUNT = COUNT + 1

\(\text{ABS}(S - S_2) < \epsilon\) \(\Rightarrow\) NO

\(\text{COUNT} > 40\) \(\Rightarrow\) NO

\(\text{COUNT} > 15\) \(\Rightarrow\) YES

"WILL NOT CONVERGE"

\(S_2 = S + \text{DAMP}(S_2 - S)\)

\((CF_2)_{i+1} = y_2(1 - f) + x_2 f\)

\((CF_3)_{i+1} = y_3(1 - f)\)

\((CF_4)_{i+1} = x_4 f\)
production?
NO

INTEGRATE PRODUCTION

TOT2 = TOT2 + (CF2)Nx•DT
TOT3 = TOT3 + (CF3)Nx•DT
TOT4 = TOT4 + (CF4)Nx•DT

STORE PRODUCTION DATA

production?
NO

PRINT PRODUCTION HISTORY

production?
YES

call SWITCH to reverse cell location in matrix so boundary condition can be applied at x = L for the production phase.
APPENDIX D

Detailed Account of Preliminary Experimental Work

The composite core used in the confirmation experiment had been used in one previous experiment attempting to determine the extent of isopropyl acetate hydrolysis caused by water associated with the clays in reservoir rock. Prior to their original use, the seven Torpedo sandstone core plugs had been cut using water as a cooling fluid and were dried thoroughly in a vacuum oven at 250 degrees F. They subsequently were allowed to cool in a desiccator. The core plugs were then assembled into a composite core by stacking the cores end to end, wrapping them in Teflon tape and slipping two rubber sleeves over their entire length. Core end plugs were fitted on either end of the assembly. The assembled composite core model had a total length of 94.23 cm and a diameter of 3.79 cm. The entire assembly was placed inside a triaxial mounting tube. "O"-ring seals on the core end plugs formed a pressure seal which allowed the annular region between the outer core sleeve and the mounting tube to be filled with Primal 355 and pressurized to 2500 psig. This was done to simulate overburden pressure on the composite core. The triaxial mount was then placed in a water bath and allowed to equilibrate at 90 degrees C while the core itself was placed under a vacuum. An Artic diesel mixture containing 10% isopropyl acetate and 0.1% isopropyl alcohol was admitted to the system using a Ruska pump in conjunction with a floating-piston transfer vessel. The total volume admitted was 256cc which should roughly approximate the total composite system pore volume.
The core was shut in for nine days while being maintained at 90 degrees centigrade and was then produced using Arctic diesel as a displacing fluid. The core was later removed from the mount and left on a countertop for a period of three months. During this time both ends of the core were exposed to the atmosphere through the core end plugs.

This core assembly was believed to be water free. As such, it was chosen for the confirmation experiment, because it could be easily restored to connate water saturation conditions. The composite model was reinserted to the triaxial mounting tube, and again, the annular region was filled with Primol 355 and pressurized to 600 psig. The apparatus shown in Figure D.1 was then constructed for the purpose of a pore volume determination experiment. First, a total of 370 cc Arctic diesel was pumped through the composite model in hopes of removing any air that may have been trapped in the system. A single component tracer test was then performed to establish the pore volume. The core was bled to atmospheric pressure, a 5.0 cc slug of pure isopropyl alcohol was injected into the upstream end of the core using the tracer injection syringe. The core was then repressurized to 270 psig. The alcohol slug was pushed through the composite model with Arctic diesel at an initial rate of 66 cc/hr. Samples were taken downstream of the core using the sampling system shown in Figure D.2 in order to determine the mean residence time of the isopropyl alcohol. This sample loop could be alternately filled with effluents from the core or be flushed with Arctic diesel to drive the isolated sample into a collection bottle. The sample loop was flushed with 0.50cc Arctic diesel, and the sample collected in 1 cc graduated sample vials. 40 μl of distilled water was injected into each vial using a spring-loaded Hamilton syringe.
Sampling System in Loop-Filling Position

Sampling System in Loop-Flushing Position

FIGURE D.2
The sample was shaken vigorously for approximately 15 seconds and then placed in a centrifuge to assist phase separation. 2 μl samples of the aqueous extract were analyzed with a gas-chromatograph to determine the alcohol content.

Several problems related to the experimental technique made the results from this experiment difficult to analyze. First, the partitioning coefficient of isopropyl alcohol in water with respect to oil is such that the concentrations in the extract were so high that the chromatograph electrometer became saturated and displayed a non-linear response. Also at higher concentrations, there is a large dependence of the partitioning coefficient on concentration. Additionally, the sample loop volume was actually 0.635 cc. Consequently, the entire loop was not being flushed and some cross contamination of samples occurred. Another problem was that the core had to be depressurized and repressurized during the tracer injection procedure. These problems were considered significant enough to repeat the test. Nevertheless, a rough calibration was produced by analyzing the extracts from a series of Arctic diesel solutions of known concentrations. This calibration was utilized to make a better approximation of the actual alcohol concentration in the produced oil. A mean retention time for the alcohol slug of 276.5 cc was calculated using the resulting corrected concentration data. If no water were present, this figure would represent the pore volume of the composite model.

A second attempt was made to determine the model pore volume. An improved tracer slug injection system was incorporated into the apparatus so that the slug could be introduced without disturbing either the system pressure or flow behavior. The new injection system
consisted of a six-port Valco valve with adjacent entry and exit ports connected in a suitable fashion to allow a 5.0 cc capacity tracer slug loop to be flushed and filled while the flowing fluids bypassed the injection loop. The tracer slug could be introduced to the flowstream by turning the valve stem. To alleviate the problems of non-linear chromatographic response and non-constant partitioning coefficients present at higher alcohol concentrations a 1% isopropyl alcohol in Arctic diesel solution was used as the tracer slug. Additionally, 0.75 cc Arctic diesel was used to displace the collected samples entirely out of the sampling system so that no cross-contamination of the samples would occur.

The production history from this test was dramatically different from that of the first test. The apparent mean retention volume of the alcohol was almost 100 cc greater than in the previous test. The retention volume was obviously greater that the pore volume of the composite model, and as such, it indicated that some water was probably present in the core as water would have a tendency to retard the progress of the alcohol through the porous medium. This experiment did not give any indication of the composite system's effective pore volume, but it did show that some water was present in the core.

A third tracer test was performed to establish the water saturation of the core and to establish a pore volume for the model. Two different tracers, with widely different partitioning coefficients were used in this test: isopropyl alcohol and methyl isobutyl ketone. The general method used was developed by Deans and Shallenberger. As the methyl isobutyl ketone, hereafter refered to as MIBK, has little tendency to partition into the aqueaus phase, it tends to flow
at the velocity of the oil phase. Its retention volume will represent
the volume of oil in the pore space. Conversely, isopropyl alcohol,
IPA, has a strong tendency to partition into the aqueous phase.
Consequently, the alcohol will display a slower effective velocity
through the model since the aqueous phase is not mobile. The probabi-
ity if the IPA residing in the non-flowing aqueous phase increases as
the saturation of that phase increases. Hence, the observed residence
time will be increased as the saturation increases. The Deans-
Shallenberger method applies the principles of chromatography to utilize
the different tracer component residence times to predict the fluid
saturations present in the core. Once the saturation is known, a
total pore volume can be calculated using the mean residence time of
MIBK to represent the oil phase volume along with a small correction to
account for the slight retardation of the MIBK by the aqueous phase.

The third tracer test was run at a constant flowrate of 66 cc/hr
at room temperature and 270 psig. 14 cc Arctic diesel were pushed
into the model to establish steady state flow. At this point, a 5.0 cc
slug of 1% IPA and 1% MIBK in Arctic diesel was introduced using the
tracer slug injection system. Samples were taken on an occasional
basis until the first traces of the IPA slug appeared and roughly every
6 cc thereafter.

K-values or partitioning coefficients were determined by mixing
an amount of the trace component with a suitable amount of water to
approximate the average concentration of the component in the extract
from the experimental samples. This solution was then chromatographic-
ally analyzed. An amount of oil calculated to extract approximately
half (based on previous rough determinations of the partitioning
behavior) of the component from the water phase was added. The mixture was shaken vigorously and repeatedly. The extract was then heated to determine how much of the trace component remained. This information along with the volumes of the water and oil used in the experiment are sufficient to calculate the partitioning coefficient which represents the ratio of the component concentration in the aqueous to that in the oil phase. Since nothing was known of the water in the core, it was assumed to be salt-free and the K-values were determined accordingly.

The mean residence volume for the MIBK and IPA were 273.7 cc and 369.1 cc after corrections were made for dead volume in the system. This indicates that a 0.9% saturation of water existed in the core and that the pore volume of the core model was approximately 276 cc. This indicated the presence of 2.5 cc water in the core model.

The composite model was then flooded with a 5% NaCl brine to establish an appreciable water phase saturation. The brine was introduced into the model by means of a Ruska pump in conjunction with a floating piston transfer vessel. Produced fluids flowed from the core through a back pressure regulator and into a separator (graduated). The produced oil collected in the separator while produced brine flowed out from the bottom of the separator into a collection flask. During the brine flood, pure oil was displaced out the model until brine breakthrough. After that point, little oil was produced. The oil produced represents the amount of brine captured by the core (after corrections are made for dead volume). The volume of oil displaced indicates that 206.8 cc brine remained in the core.

During this final flooding with oil, two tracer tests were
performed to confirm the previously established pore volume and to
determine the fluid saturations present in the model. Both
tests were run with 5.0 cc slugs of Arctic diesel containing MIBK
and n-butanol in trace amounts. The first of these tests showed
mean residence times of 206.7 and 432.7 for the MIBK and n-butanol
respectively. The second test showed retention times of 212.5 and
430.2 for the two trace components. K-values were determined by the
method described above with the exception that a 5.0% NaCl brine was
used in place of the water. The K-values were determined to be 17.36
and 0.278 for MIBK and n-butanol. This information indicates that the
apparent saturation of the aqueous phase was 23.9 percent and 22.7
percent. These values are in close agreement with those based on
the volumetric measurements as is shown in Table D.1. The pore
volume indicated by these two experiments were 266.8 and 270.3 cc.
### TABLE D.1

Summary of Preliminary Experimental Work

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Tracer</th>
<th>Mean Resid. Volume</th>
<th>$K_i = \frac{c_o}{c_w}$</th>
<th>$S_w$ %</th>
<th>Pore Volume</th>
<th>Apparent Water Volume</th>
<th>Oil Displaced</th>
<th>Brine Displaced</th>
<th>Total Water</th>
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<td>MIBK</td>
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<tr>
<td>Trcr Test #4</td>
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<td>17.36</td>
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<td>266.8</td>
<td>63.8</td>
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<td>65.2</td>
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<td></td>
<td></td>
<td></td>
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<td>206.8cc</td>
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</table>
REFERENCES


(10) Determination of Residual Oil Saturation, (Interstate Oil Compact Commission, Oklahoma City, OK, June 1978)