

Single-Well Tracer Method To Measure Residual Oil Saturation

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Introduction

Residual oil saturation is a basic item of data for many aspects of reservoir engineering. This number is required for normal material-balance calculations. Residual oil saturation is also extremely important in determining the economic attractiveness of a planned waterflood or a proposed tertiary recovery operation. Finally, in some areas proration is related to attainable residual oil saturation.

Core analysis and well logging, the two most widely used methods for measuring residual oil saturations, are subject to a variety of well known limitations. One principal common fault is that both methods yield values that are averages over very small reservoir volumes. The chemical tracer method described in this paper samples a much larger volume of reservoir around a single well. The residual oil saturation measured represents an average over as much as several thousand barrels of pore space. Because this method makes an in-situ measurement, additional limitations of other methods are also avoided.

In the single-well tracer technique, a primary tracer bank consisting of ethyl acetate tracer dissolved in formation water is injected into a formation that is at residual oil saturation. This bank is followed by a bank of tracer-free water. The well is then shut in to permit a portion of the ethyl acetate to hydrolyze to form ethanol, the secondary tracer. Finally, the well is produced and the concentration profiles of the two tracers are monitored.

Ethyl acetate is soluble in both the water and oil phases, but ethanol is, for all practical purposes, soluble only in the water phase. As a result, the ethanol travels at a higher velocity and returns to the wellbore earlier than does the ethyl acetate. The difference in arrival times can be used to determine the residual oil saturation through the use of computer programs that simulate the tracer test (the greater the oil saturation, the greater the difference in arrival times). Field tests have demonstrated the reliability and applicability of this technique.

This paper describes the tracer method, gives results of field experience, and presents a mathematical description of the process. One field application is described in detail, followed by a discussion of the scope and limitations of the technique.

General Description of the Tracer Method

Theoretical Basis

The chemical tracer method depends on chromatographic retardation of a tracer chemical that is soluble both in formation water and in oil. Considering a system in which the oil is stationary (or at residual saturation) and the formation water is flowing at a velocity \vec{v}_{w0} , the local velocity of a typical tracer molecule is

$$\vec{v}_i = \vec{v}_{wfwi}, \dots \dots \dots (1)$$

A new single-well tracer method has been developed to measure residual oil saturations of watered-out formations within a precision of 2 to 3 PV percent. This in-situ method makes an average measurement over a large reservoir volume by using trace chemicals dissolved in formation water. The technique is applicable in both sandstones and limestones for a wide range of conditions.

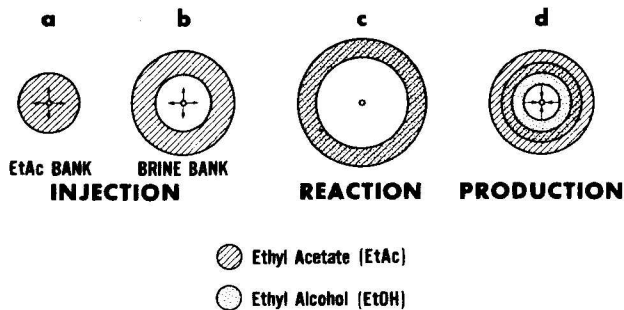


Fig. 1—Schematic representation of test procedure.

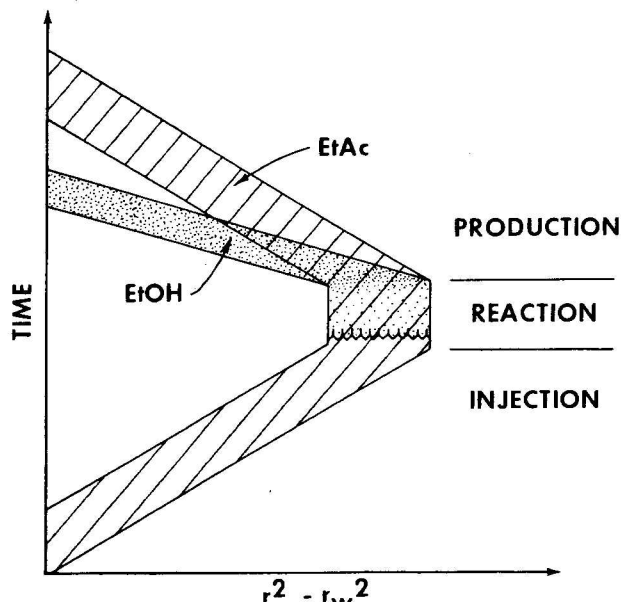


Fig. 2—Trajectories of the tracer banks.

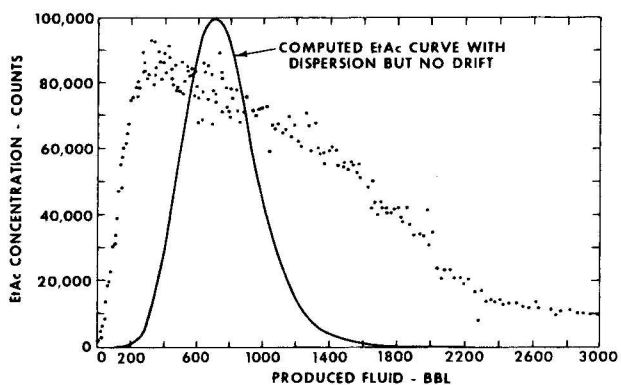


Fig. 3—Comparison of ethyl acetate data from first test with computed no-drift curve.

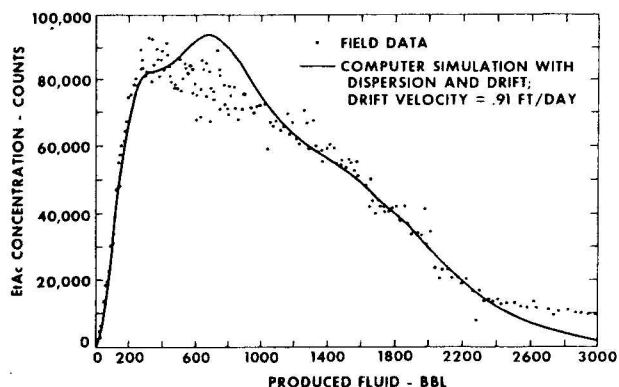


Fig. 4—Computed ethyl acetate curve for the first test with drift.

where f_{wi} is the fraction of time the tracer molecule spends in the water phase. If \vec{v}_{iw} is sufficiently small that the tracer distribution between the oil and water phases is near equilibrium, f_{wi} is given by

$$\frac{1 - f_{wi}}{f_{wi}} = \frac{k_i S_{or}}{1 - S_{or}} \equiv \beta_i, \dots \dots \dots (2)$$

where k_i is the equilibrium distribution coefficient, defined as the ratio of the tracer concentration in the oil phase to that in the water phase at equilibrium; and S_{or} is the residual oil saturation as a fraction of pore volume. By solving Eq. 2 for f_{wi} and then substituting in Eq. 1, the velocity of a typical tracer molecule can be written as

$$\vec{v}_i = \frac{\vec{v}_w}{1 + \beta_i}, \dots \dots \dots (3)$$

where $\frac{1}{1 + \beta_i}$ is the retardation factor.

Using similar arguments, two tracers with different distribution coefficients, k_1 and k_2 , will have different local velocities, \vec{v}_1 and \vec{v}_2 . Therefore, separation of tracers can occur in the reservoir in a manner analogous to that in a chromatographic column.

Development of the Single-Well Method

Previous investigators¹ have shown that the predicted retardation of a solute based on the assumption of equilibrium mass transfer appears to be correct for flow through reservoir rock at typical rates. Cooke² proposed a between-well test and a test involving vertical flow between two perforated intervals in a single well, both of which use two tracers with different distribution coefficients to measure residual oil saturation. Although these tests have definite application in special circumstances, a more practical single-well technique is preferred.

Two tracers having different distribution coefficients separate as they leave the wellbore and flow into a formation with residual oil saturation. If the direction of flow is later reversed by producing from the same well, the separation disappears as the tracers return to the wellbore. This reversibility appears to make a single-well procedure unworkable. Another technique based on differences in dispersion (mixing) rather than on differences in tracer velocities has been proposed. It was concluded that this technique is not sensitive enough to permit reliable measurement of residual oil saturations.³

The method described here avoids the problem of reversibility by taking advantage of an irreversible chemical reaction to produce the second tracer in situ.⁴ Laboratory work demonstrated that ethyl acetate would hydrolyze at a sufficiently high rate in neutral brine solutions at typical reservoir temperatures. Also, laboratory measurements of the equilibrium distribution of ethyl acetate between crude oil and brine gave distribution coefficients in the range of 5 to 8. Ethanol, one of the products of the ethyl acetate hydrolysis, was found to have an equilibrium distribution coefficient of essentially zero

(< 0.1). This means that, for flow through a reservoir with a residual oil saturation of 10 to 20 PV percent, the velocity of ethyl acetate is on the order of one-half the velocity of the water phase or of the ethanol. A velocity difference of this magnitude is optimal. A smaller difference results in poor separation of the tracers; a larger difference means that the distance travelled by the ethyl acetate is reduced, thus limiting the volume of reservoir sampled.

On the basis of laboratory results, the following scheme was developed for measuring residual oil saturation in situ with a single-well test. The primary tracer solution, ethyl acetate dissolved in formation water at a concentration between 0.5 and 2.0 percent by volume, is injected as a bank and is then displaced into the reservoir by a bank of injected brine. This procedure is shown schematically in Figs. 1a and 1b. (Compounds other than ethyl acetate can be used as the primary tracer, but ethyl acetate appears to be best suited for most applications.) After injection, the well is shut in for 1 to 2 weeks. During this time, some of the ethyl acetate hydrolyzes to form ethanol. Chemical reaction can be thought of here as a distributed source for ethanol, the secondary tracer. The condition in the reservoir at the end of the reaction phase is illustrated in Fig. 1c.

When sufficient reaction time has elapsed, the third phase of the tracer test is begun. The well is produced until all the injected fluids have been recovered. Samples are taken periodically, sealed, and preserved at low temperature to avoid ethyl acetate loss by evaporation or reaction. Using gas chromatography, the concentrations of ethyl acetate and ethanol in the samples are measured to define the production profiles for these tracers. As illustrated in Fig. 1d, the ethanol returns to the well ahead of the unreacted ethyl acetate. The difference between the arrival times for the two tracers is directly related to residual oil saturation.

The trajectories of the tracer banks are shown in Fig. 2. This plot of time vs the square of the radial distance from the wellbore is for a cylindrical geometry that features a well fully penetrating a homogeneous stratum with barriers above and below. Both tracer banks retain their shape in radius-squared direction throughout the test. Because of its greater velocity, however, the returning ethanol bank is compressed on the time axis. Since concentrations are measured at the wellbore as a function of time, this compression can be observed. It is also directly related to the residual oil saturation. Fig. 2, although very informative, is an idealized representation of a tracer test in that it neglects dispersion and assumes that all the chemical reaction occurs during the shut-in period.

Theoretical Insight Gained Through Field Experience

The method described above has been successfully used to measure residual oil saturation in four different fields. In each case, the field test contributed to our understanding of the tracer method. The qualitative features of each test are given below; the third test is described in more detail in a later section.

The first test was run in a watered-out sandstone stratum about 20 ft thick. Slightly more than 1,000 bbl of fluid was injected. In this first test and in all succeeding tests, both the primary tracer bank and the displacing brine bank contained methanol for use as a material-balance check and to assist in estimating dispersion. Simplified calculations, made during the reaction phase, indicated that fluid migration in the formation due to reservoir water drive might displace the tracer banks while the well was shut in. Consequently, production was begun after a reaction period of only 9 days. The fear that the fluid drift might distort tracer production profiles was justified. Fig. 3 qualitatively compares the measured ethyl acetate profile with a calculated curve that assumes no drift. Fig. 4 shows the improvement in the calculated results when the appropriate drift velocity is included in the simulation. The movement of the ethyl acetate bank in the presence of fluid drift is illustrated in Fig. 5. As shown, the tracer banks no longer remain centered about the wellbore as in the case when drift is negligible.

The second test was also conducted in a sandstone reservoir. In this case, it was decided to perform a small-volume (100 bbl of injected fluid) preliminary test to debug field procedures and to obtain better estimates of drift and reaction rate for use in designing a main test. The practice of running a "minitest" has been continued; the added cost is small and the information gained is valuable.

Fluid drift was not a significant factor in the second test. The quality of the data was greatly improved over that of the first test, and the residual oil saturation was determined with more precision. Also, gas lift was shown to be an acceptable method for producing wells during a tracer test despite the fact that the ethyl acetate is quite volatile. The ethyl acetate profile that was measured using samples collected down hole (below the gas-lift valves) is compared in Fig. 6 with the calculated curve. The profile obtained from the analysis of samples of the liquid leaving the

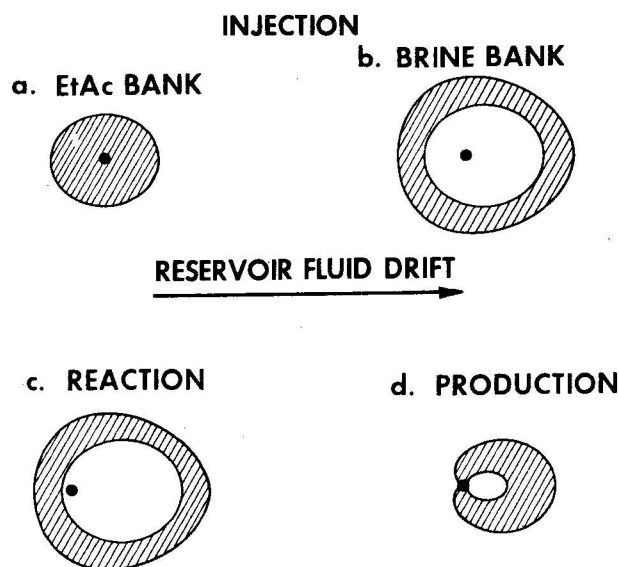


Fig. 5—Effect of drift on the movement of the ethyl acetate bank.

surface separator is similar but is attenuated by losses of tracer to the lift gas.

The third test was designed to be identical with the second test with one exception. The concentration of ethyl acetate in the primary tracer bank was increased in an attempt to improve the accuracy of the chromatographic analyses. Primarily as a result of the higher ethyl acetate concentration, two non-linear effects were observed for the first time. The first effect is that the distribution coefficient depends on concentration as well as on temperature and brine salinity. Fig. 7 shows this dependence. The second effect is that the residual oil phase swells as a result of mass transfer of ethyl acetate from the water to the oil phase. Fig. 8 compares the field data for the main test with two calculated curves — one that accounts for the nonlinear effects and one that neglects them. Although the quality of the match is improved by including the nonlinear effects, the measured residual oil saturation is not significantly affected.

The fourth test was the first to be conducted in a limestone formation and was also the first to use a submersible electric pump for the production phase. No major problems were encountered. Drift was shown to be a factor in the main test. The ethyl acetate data from the main test and the computed profile are shown in Fig. 9. Fig. 10 illustrates that measured concentration profiles for methanol — the material-balance tag — can be fitted with computed curves based upon the same values of drift velocity and dispersion used to match the profiles for ethyl acetate. Thus, matches between the field and computed results form a consistent test description.

Mathematical Description of the Tracer Method

General Model

The assumptions made in deriving the mathematical model of a tracer test are: (1) the fluids are incompressible, (2) the oil phase is immobile, (3) chemical reaction occurs only in the brine phase, (4) equilibrium mass transfer is achieved, (5) the tracer mass flux is small compared with the mass flow rate of water, and (6) the formation is homogeneous and

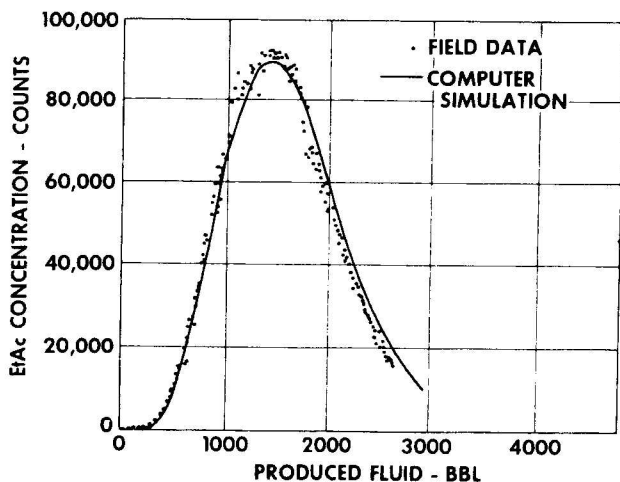


Fig. 6—Ethyl acetate field data and computed curve for the second test.

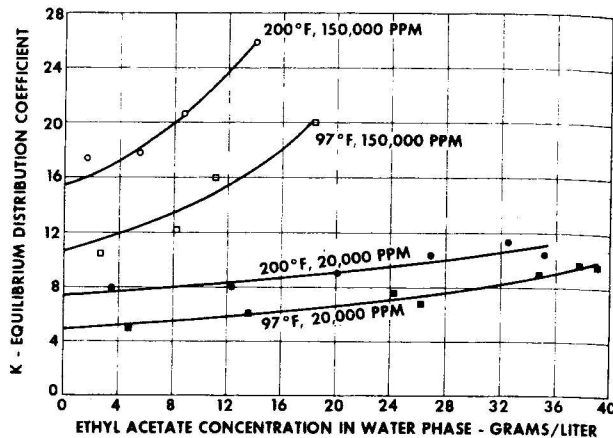


Fig. 7—Equilibrium distribution coefficient as a function of acetate concentration for various brine salinities and temperatures.

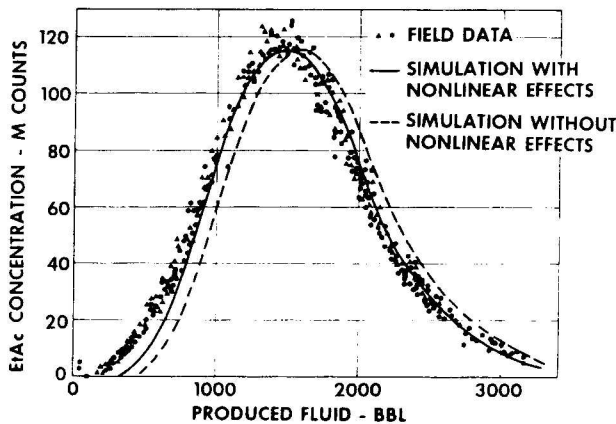


Fig. 8—Influence of nonlinear effects.

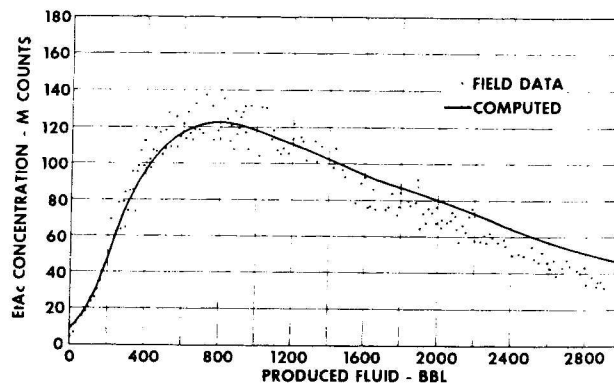


Fig. 9—Ethyl acetate concentration profile from the fourth test.

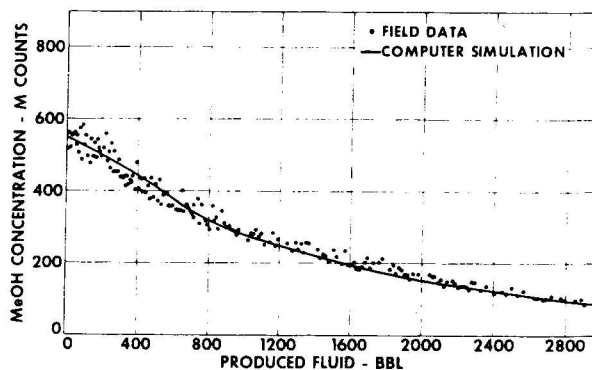


Fig. 10—Methanol concentration profile from the fourth test.

isotropic. The velocity field for the flow of formation water must satisfy the total continuity equation,

$$\vec{\nabla} \cdot (S_w \vec{v}_w) = 0 \quad (4)$$

The concentration of each tracer component obeys the component continuity equation,

$$\begin{aligned} \frac{\partial}{\partial t} (S_w C_i + S_o \bar{C}_i) + \vec{\nabla} \cdot (S_w C_i \vec{v}_w) \\ + S_w R_i (C_1, \dots, C_i, \dots, C_N) \\ = \vec{\nabla} \cdot (S_w \underline{K}_e \cdot \vec{\nabla} C_i), \quad i = 1, N, \dots \end{aligned} \quad (5)$$

where

- C_i = concentration of tracer component, i , in the water phase,
- \bar{C}_i = concentration of tracer component, i , in the oil phase,
- R_i = rate of production of tracer component, i , by chemical reaction; in general, a function of tracer concentrations ($C_1, \dots, C_i, \dots, C_N$), and
- \underline{K}_e = the effective dispersion tensor in the porous medium, a function of \vec{v}_w .

In addition, an equation relating the equilibrium tracer concentrations in the oil and water phases is needed:

$$\bar{C}_i = f_i(C_i) \quad (6)$$

And the oil saturation must be described as a function of the residual oil saturation and tracer concentrations in the oil phase:

$$S_o = S_o(S_{or}, \bar{C}_1, \dots, \bar{C}_i, \dots, \bar{C}_N) \quad (7)$$

Tracers are assumed to be absent initially. Boundary conditions are imposed on tracer concentrations at the wellbore during the injection phase.

Numerical Procedures

The residual oil saturation is obtained by matching the measured concentration profiles with a numerical simulation of the test. Two different simulators have been developed; both solve the equations constituting the mathematical model using finite-difference techniques. One simulator assumes one-dimensional flow and is limited to those cases where fluid drift is negligible. The other is a two-dimensional simulator, which is used where drift must be accounted for. The two-dimensional model does not include swelling of

TABLE 1—MAIN PARAMETERS FOR THIRD FIELD TEST

	Minitest	Main Test
Injection rate, B/D	995	999
Volume of EtAc bank, bbl	85	550
Volume of push bank, bbl	85	1,370
Total injected volume, bbl	170	1,920
Injected EtAc concentration, volume percent	1.0	1.5
Injected MeOH concentration, volume percent	0.5	0.5
Shut-in period, days	3	12
Production rate, B/D	752	857

the oil phase. However, this effect is normally less important than the concentration dependence of the distribution coefficient, which is included in both simulators.

In addition to the simulators used in test interpretation, special computer models have been developed to account for mobile oil and for stratification of the test interval. Limited runs performed to date indicate that the test procedure is surprisingly insensitive to these effects.

Application of the Method

General Test Description

The third field test mentioned earlier was run in a 20-ft-thick sandstone stratum. The temperature at the perforated interval was 170°F. Native formation water, which was used as a solvent for the injected tracers, had a measured salinity of 120,000 ppm. On the basis of the rate of movement of the water-oil contact farther updip, little drift was anticipated. Both a main test and a minitest were performed; gas lift was used as a means of artificial lift in both cases. All of the injected fluid was tagged with methanol. The main parameters describing the tests are listed in Table 1.

An electric log of the well showing the test interval is shown in Fig. 11. The average permeability of the test interval, as measured by a pressure fall-off test, was 490 md. The viscosity and formation volume factor for the oil at reservoir conditions were 0.6 cp and 1.27 RB/STB, respectively.

Simulation of the Test

Down-hole samples of the crude were collected from nearby wells, and the formation water was sampled. These fluids were then used in making laboratory measurements of the equilibrium distribution coefficient for ethyl acetate at reservoir conditions. The

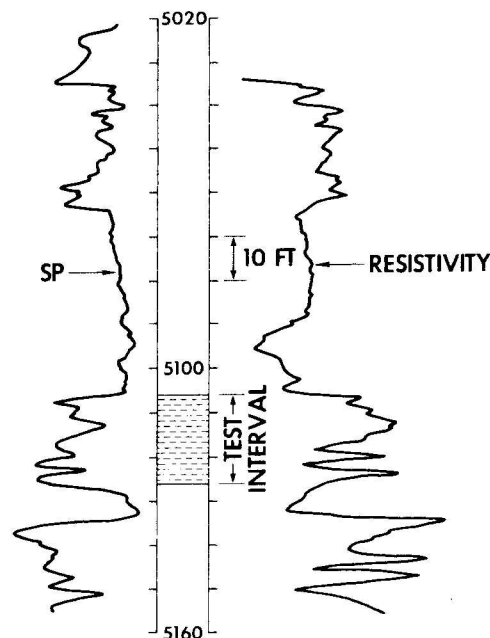


Fig. 11—Electric log of the test interval for the third test.

equilibrium relationship is described by the following expression:

$$\bar{C}_{\text{EtAc}} = \frac{7.4 C_{\text{EtAc}}}{1 - 0.020 C_{\text{EtAc}}}, \quad (8)$$

where concentrations are expressed in grams per liter.

Since drift was apparently not a factor in the third test, the test could be simulated using the one-dimensional radial flow model. For this model, the interstitial velocity field that satisfies Eq. 4 is given by

$$v_{wr} = \frac{5.615 Q}{2\pi r h \phi S_w}, \quad (9)$$

where $Q > 0$ for injection, and $Q < 0$ for production. Eq. 5 for ethyl acetate is

$$\frac{\partial}{\partial t} (\bar{S}_w C_{\text{EtAc}} + S_o \bar{C}_{\text{EtAc}}) + S_w v_{wr} \frac{\partial C_{\text{EtAc}}}{\partial r} - S_w k C_{\text{EtAc}} = \frac{1}{r} \frac{\partial}{\partial r} \left(r S_w K_r \frac{\partial C_{\text{EtAc}}}{\partial r} \right), \quad (10)$$

and for ethanol is

$$\frac{\partial}{\partial t} (S_w C_{\text{EtOH}}) + S_w v_{wr} \frac{\partial C_{\text{EtOH}}}{\partial r} + S_w k C_{\text{EtAc}} = \frac{1}{r} \frac{\partial}{\partial r} \left(r S_w K_r \frac{\partial C_{\text{EtOH}}}{\partial r} \right), \quad (11)$$

The ethyl acetate hydrolysis is assumed to be first order in the acetate concentration with rate constant, k . Eq. 8 is used to describe the equilibrium distribution of ethyl acetate, and the function defined in Eq. 7 is

$$S_o = 1 - S_w = \frac{S_{or}}{1 - \bar{v}_{\text{EtAc}} \bar{C}_{\text{EtAc}}}, \quad (12)$$

where \bar{v}_{EtAc} is the laboratory-determined swelling coefficient (molar volume) for ethyl acetate.

Finally, the radial dispersion coefficient is assumed to be directly proportional to the magnitude of local interstitial velocity:

$$K_r = \alpha |v_{wr}|, \quad (13)$$

Concentration and flow-rate histories for the injection and production phases of the test, the duration of the shut-in period, and the porosity-thickness product of the formation are fixed-input data to the simulation. Input parameters that are varied to achieve the best fit of the field data are (1) S_{or} , the residual oil saturation (the test objective), (2) k , the hydrolysis rate constant, and (3) α , the constant in Eq. 13, the equation for the radial dispersion coefficient.

Results of Test Interpretation

The quality of the field data from the third test was quite good. The best fit of the tracer production profiles measured in the main test was obtained with a residual oil saturation of 19 PV percent. The precision of this value was estimated to be ± 2 PV percent. Fig. 12 shows the quality of the match between measured ethyl acetate data, based on both surface and down-hole samples, and the computer simula-

tion. (The amplitude of the down-hole data shown in the plot has been reduced by a constant factor that is related to the ethyl acetate loss to the lift gas.) The match between field data for methanol and the simulator results is illustrated in Fig. 13. Ethanol data are compared with computed curves for residual oil saturations of 18, 19, and 20 PV percent in Fig. 14. Fig. 15 shows a corresponding match of the minitest data. The residual oil saturation measured in the minitest was 18 ± 3 PV percent. Although the purpose of the minitest was primarily to debug operating procedures, minitest data proved to be of sufficiently good quality to permit interpretation. Good agreement between the two measurements indicates not only that the procedure is repeatable, but also that estimates of the precision that can be expected are reasonable. Because the main test samples a much larger volume of reservoir than does the minitest, the agreement also indicates little flushing of oil from the region around the wellbore. Residual oil saturations measured by the chemical tracer test are within the range of values (11 to 23 PV percent) measured by waterflooding preserved cores, but are higher than those (6 to 10 PV percent) obtained by vacuum distillation of cores cut with a pressure core barrel.

Laboratory Confirmation of Accuracy

Conventional methods for determining residual oil saturation cannot be considered as accepted standards for use in determining the absolute accuracy of the tracer technique. However, tracer measurements have generally fallen within the broad range of residual oil saturations obtained from core tests. The relative accuracy or precision, estimated by examining the sensitivity of the measured oil saturation to changes in input to mathematical model, appears to be ± 2 to 3 PV percent. Moreover, the reliability of the method, as determined by comparing minitest results with those from the main test, is within the same range.

Laboratory results can be used to confirm the accuracy of the tracer method and to verify the theory. One experiment is typical of laboratory results obtained. In this case, a composite core from a limestone formation was waterflooded to residual oil. The residual oil saturation measured by volumetric balance was 30 ± 3 PV percent. On the basis of a linear tracer test on the core, the oil saturation was computed to be 29 ± 2 PV percent. Thus, the two measurements agree within the precision of the measurement techniques.

Scope and Limitations of the Method

The single-well chemical method can be used to make in-situ measurements of residual oil saturation in either sandstone or limestone formations over a wide range of temperatures, water salinities, and residual oil saturations. In the four field tests, formation temperatures and salinities ranged from 140° to 200°F and from 400 to 120,000 ppm, respectively, and residual oil saturations of 10 to 20 PV percent were measured. The range of applicability is much broader and can certainly be extended in future tests. If artificial lift is needed, the well can be produced using

ther gas lift, rod pump, or submersible electric pump.

The chemical tracer method gives a reasonably precise measurement of residual oil saturation. Moreover, the measured value represents an average over the volume of reservoir invaded by the ethyl acetate bank — a substantial volume as opposed to a point measurement in the wellbore.

The reversible nature of the flow pattern permits the test to be used in reservoirs that are considerably stratified. However, the higher-permeability zones are weighted more heavily in measuring an average residual oil saturation. In one example where drift was significant, the effect of stratification on test interpretation was examined by subdividing the test interval into four different layers. When the test was simulated using the four-layer model, the computed concentration profiles were almost identical with those obtained using the single-layer or "homogeneous" model. Moreover, the permeability-thickness weighted average of the oil saturation values for the four layers was equal to the oil saturation obtained using the single-layer model. It is more difficult to determine exactly how heterogeneities other than stratification affect test interpretation. However, analogous to the interpretation of single-well buildup and fall-off tests using a homogeneous model, the simulators that assume a homogeneous model should be suitable for interpreting single-well tracer tests where there are no gross formation heterogeneities. Furthermore, any gross heterogeneities can be detected by running a pressure test either before or in conjunction with the tracer test.

The chemical tracer method described here has certain limitations that should be kept in mind. The mathematical description presented in this paper is applicable only for a formation that is at a residual oil saturation; however, a general model could be developed to interpret tests conducted in formations containing mobile oil. It may not always be practical to conduct tests in wells with large intervals open to the wellbore or with large holdup volumes in the wellbore. Thus, workovers may be required in some cases to prepare a well for the test. The test data become more difficult to interpret in the presence of a large amount of fluid drift. However, this can be recognized in a minitest, and the main test can be planned to minimize the effect of drift.

conclusions

1. A new single-well chemical tracer method has been developed for measuring residual oil saturation in situ. The technique has been proved in practice through its use in four field tests.
2. Residual oil saturations are determined by matching field-measured data using computer programs for simulating the tracer test. Because the simulation programs account for all important aspects of the theory — including drift, dispersion, reaction, and minor nonlinear effects — residual oil saturations have been repeatedly measured with a precision of 2-3 PV percent.
3. The tracer method has a wide range of applicability. Production can be by gas lift, by rod pump, or

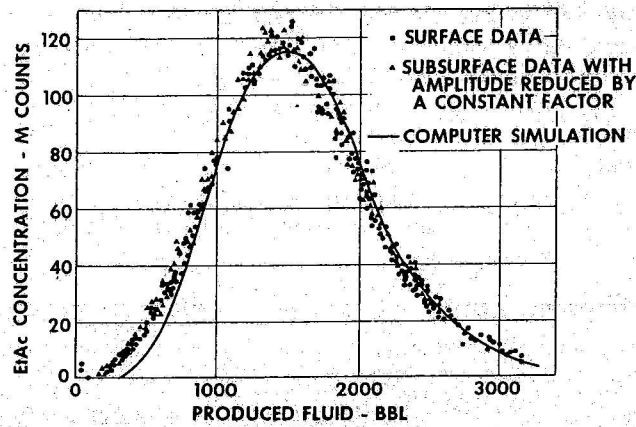


Fig. 12—Ethyl acetate concentration profile from the third test.

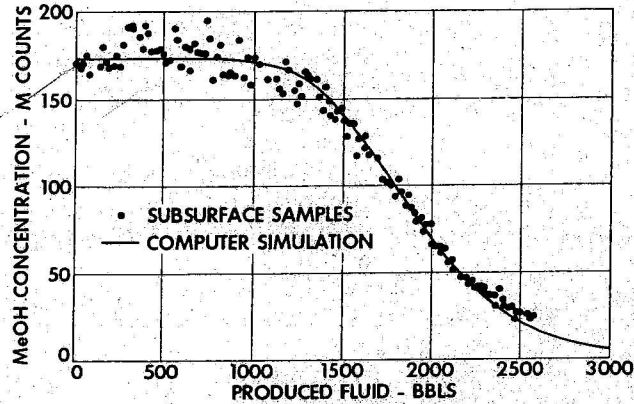


Fig. 13—Methanol concentration profile from the third test.

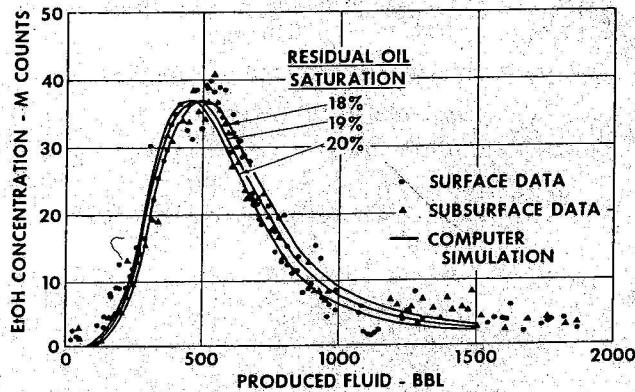


Fig. 14—Ethanol concentration profile from the third test.

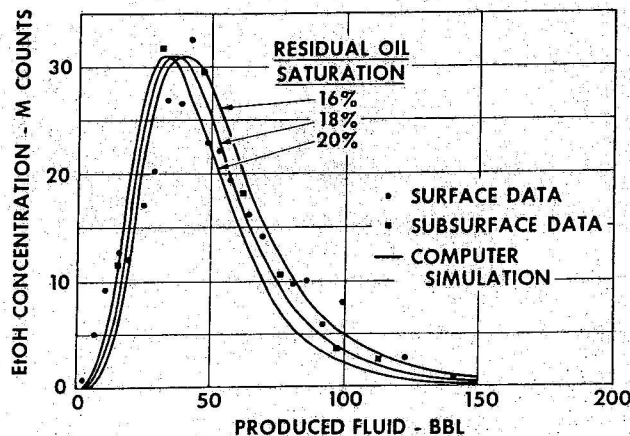


Fig. 15—Ethanol concentration profile from the minitest.

by submersible electric pump. Field experience has involved a wide range of formation temperatures, water salinities, and residual oil saturations.

4. Small-volume pretests, called minitests, are useful for debugging field procedures and for providing field measurements of parameters for use in designing the main test. In many cases, minitest data can also be analyzed to give a quantitative estimate of residual oil saturation.

Nomenclature

- C_i = concentration of tracer component, i , in the water phase
 \bar{C}_i = concentration of tracer component, i , in the oil phase
 \underline{K}_e = effective dispersion tensor in the porous medium
 K_r = effective radial dispersion coefficient
 f_{wi} = fraction of flow time that tracer component i spends in the water phase
 h = formation thickness
 k = reaction-rate constant
 k_i = equilibrium distribution coefficient for tracer component i
 Q = well rate (positive for injection, negative for production)
 r = radial coordinate
 R_i = reaction rate for tracer component, i
 S_o = oil saturation
 S_{or} = residual oil saturation
 S_w = water saturation
 t = time
 \tilde{v}_i = swelling coefficient (molar volume) for tracer component, i
 \vec{v}_i = local velocity of tracer component, i
 \vec{v}_{w} = local interstitial velocity of the water phase
 v_{wr} = radial component of \vec{v}_w
 α = constant in dispersion coefficient expression
 β_i = constant defined by Eq. 2 for tracer component, i

ϕ = porosity

Subscripts

- EtAc = ethyl acetate
 EtOH = ethyl alcohol (ethanol)
 i = general tracer component
 N = total number of tracer components
 o = oil phase
 r = radial direction
 w = water phase
 $=$ = tensor

Superscripts

- \rightarrow = vector
 $\underline{\quad}$ = oil phase

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