ABSTRACT: A method for determining fluid saturations in a subterranean reservoir formation containing one mobile fluid phase and one or two substantially immobile fluid phases. A carrier fluid which is miscible with the mobile fluid and substantially insoluble in the immobile phase or phases is injected into the formation at one location and displaced through the formation to a second location. The carrier fluid contains two or more tracers having different partition coefficients between the carrier fluid and immobile phase or phases. As the carrier fluid moves through the reservoir, one of the tracers is retarded more than the other due to its higher solubility in the immobile phase and the tracers separate. The degree of separation of the tracers is related to the quantities of mobile and immobile fluids in the reservoir. By monitoring formation fluids at the second location to detect the presence of the tracers, the relative fluid saturations can be determined using chromatographic analytical techniques.
METHOD OF DETERMINING FLUID SATURATIONS IN RESERVOIRS

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to a process utilizing a well or wells and includes the steps of testing or measuring formation fluids. More specifically, this invention relates to a method for determining fluid saturations in a subterranean reservoir penetrated by a well.

2. Description of the Prior Art
A typical oil-productive formation is a stratum of rock containing tiny interconnected pore spaces which are saturated with oil, water and gas. Knowledge of the relative amounts of these fluids in the formation is indispensable to proper and efficient production of the formation oil. For example, when a formation is first drilled it is necessary to know the original oil saturation to intelligently plan the future exploitation of the field. In tertiary recovery techniques, such as in solvent flooding, the quantity of oil present in the formation will often dictate the most efficient manner of conducting such an operation. The concentration of oil in the formation indicate which of several alternative, tertiary recovery techniques might best be employed to produce the oil.

There are several methods which are currently used to obtain the fluid saturations of a formation. Coring is the most commonly used technique for acquiring this information. This is a direct sampling of the formation rock and liquids. For example, a small segment of the formation rock saturated with its fluids is cored from the formation and removed to the surface where its fluid content can be analyzed. This method, however, is susceptible to faults of the sampling technique; thus, the sample taken may, or may not, be representative of the formation as a whole. Also, there is a genuine possibility that the coring process itself may change the fluid saturation of the extracted core. Moreover, coring can only be employed in newly drilled wells or open hole completions. In the vast majority of wells, casing is set through the oil-bearing formation when the well is initially completed. Core samples, therefore, cannot subsequently be obtained from such a well. Finally, coring by its very nature only investigates the properties of the formation rock and fluids in the immediate vicinity of the wellbore.

Another approach for obtaining reservoir fluid saturations is by logging techniques. These techniques, also, investigate the formation rock and fluid properties for only a short distance beyond the wellbore. These techniques study the rock-fluid system as an entity; it is often difficult by this approach to differentiate between the properties of the rock and its fluids.

Material balance calculations based on production history are another approach to the problem. Estimates of fluid saturations acquired by this method are subject to even more variables than coring or logging. This technique requires a knowledge of the initial fluid saturation of the formation by some other method and knowledge of the source of the recovered fluids.

SUMMARY OF THE INVENTION

In accordance with the teachings of this invention the fluid saturations of a hydrocarbon-bearing formation are determined by injecting a fluid containing at least two tracers into the formation. The tracers have differing partition coefficients and are chromatographically retarded in their passage through the formation by different amounts. By detecting the presence of the tracers at another location in the formation and analyzing the results by chromatographic techniques, the relative proportions of formation fluids between the two locations can be determined.

Objects and features of the invention not apparent from the above discussion will become evident upon consideration of the following description of the invention taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a schematic representation of a cross section of the earth showing a subterranean formation penetrated by an injection well and a withdrawal well.

FIGS. 1B—E are schematic representations of the formation and illustrate the relative positions of two tracers as they traverse the formation.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It will be apparent from this disclosure that the method of this invention has broad applicability. The method may be employed to determine the residual oil saturation in a waterflooded formation prior to tertiary oil recovery operations.

The method may be used to determine connate water saturation in an oil or gas reservoir. The method may be used to determine the saturations of three fluid phases, gas, oil and water, coexisting in the formation. The method may employ two wells, one for injection and one for production. The method may employ a single well with fluid injected at one location in the well and fluid withdrawn from a vertically spaced second location in the same well. For purposes of clarity, however, only one of the many uses of this invention—determination of the residual oil saturation in a waterflooded reservoir—will be described in detail. The use of this method for other purposes will be readily apparent from this description.

FIG. 1A shows a subterranean oil-bearing formation lying below the surface of the earth. The formation is penetrated by an injection well 12 and a production well 13 which have been drilled from the surface. The injection and production wells have been perforated at 14 and 15 to provide fluid communication between the interior of the wells and the formation. The formation has an average thickness of 10 feet and an average porosity of approximately 25 percent. The distance between the production and injection wells is 300 feet.

The oil-bearing formation is a waterflood reservoir. Following a period of primary production operations were begun. Water was injected through the injection well, and oil and water were produced through the production well. At this point in time only minor quantities of oil are being produced; e.g., less than 1 percent oil in the produced liquids. The reservoir pressure is above the bubble point of the oil and no free gas exists in the reservoir. To determine whether tertiary recovery techniques would be economical it is necessary to know how much oil remains in the formation. The oil saturation is determined in the following manner.

A solution of two tracers in a carrier fluid is prepared at the surface. A convenient carrier liquid for use in these circumstances is brine which was previously produced from the formation. The tracers are sodium bromide, hereinafter referred to as tracer A, and sodiuryl alcohol, hereinafter referred to as tracer B. Tracer A is added to the brine at a concentration of 500 P.P.M. Tracer B is added at a concentration of 20,000 P.P.M. Two thousand barrels of the carrier liquid-tracer solution are then injected into the formation by means of the injection well at a rate of 300 barrels per day. Formation fluids are simultaneously withdrawn by means of the production well at the same rate. The carrier liquid-tracer solution is then displaced through the formation by injecting additional quantities of water through the injection well.

As shown in FIG. 1A immediately following injection, tracers A and B have been displaced from the injection well by approximately the same distance. As injection continues, however, tracer B due to its higher solubility in the formation oil begins to lag behind tracer A. As shown in FIGS. 1B—E the distance between the peak concentrations of the two tracers increases as the solution is passed through the reservoir. During this period the produced fluid from the production well is chemically analyzed for the presence of tracers A and B. After approximately 110 days tracer A breaks through at the producing well. Tracer B breaks through after 165 days.
The fluid saturations of the formation can be determined from the results of the method using the principles of chromatography. Chromatography as applied to the flow of a tracer through a porous medium is well known and has been extensively studied. See for example, Raimondi and Torcaso, "Mass Transfer Between Phases in a Porous Medium: A Study in Equilibrium," Society of Petroleum Engineers Journal, March 1965, p. 51. The results of the method can be analyzed in a number of ways by applying these principles to measured physical properties. For example, the average velocities of the tracers as they travel between the point of injection and point of detection can be used to analyze the results. In a like manner the relative arrival times of the tracers at the second location in the formation may be used. The fluid volumes, injected or produced, between the time of introducing the tracers into the formation at the first location and the time of detection at the second location may also be used. All these physical properties are measured between the introduction of the tracers at one location and the detection of the tracers at another location in the formation. Since such measured physical properties depend upon the relative chromatographic separation of the tracers, they will be collectively termed chromatographic quantities herein for convenience and clarity.

Applying the principles of chromatography to the chromatographic quantity of injected volumes in the prior example gives:

\[ S_x = \frac{V_B - V_A}{V_B - V_A} \]

where:
- \( V \) is the volume of fluid injected into the formation between the time when a given tracer is introduced at the first location and the time when the tracer is detected at the second location, barrels.
- \( K \) is the partition coefficient for the tracer between the carrier fluid and oil expressed as the mass of the tracer per unit volume of carrier fluid divided by the mass of the tracer per unit volume of oil and measured at reservoir temperature.
- \( S \) is saturation of a fluid expressed as a percent of total fluid volume of the formation.

subscripts:
- \( A \) is tracer A
- \( B \) is tracer B
- \( o \) is oil
- \( w \) is water

In the example previously illustrated, the partition coefficient for the isobutyl alcohol between the formation oil and brine at reservoir temperature is 0.85. The partition coefficient for the sodium bromide is essentially infinite since the inorganic salt is substantially insoluble in the oil phase. The volume of carrier liquid solution and following water injected prior to breakthrough of tracer A was 33,000 barrels; the volume prior to breakthrough of tracer B was 49,500 barrels. Thus, from the relationship given above it can be seen that the ratio of the oil saturation to the water saturation is 0.425. Therefore the oil saturation is approximately 29.8 percent and the water saturation is 70.2 percent.

In the illustration given above, one of the formation fluids—oil—was essentially immobile. The saturation of the oil had been reduced to a point where its flow had almost stopped. When the saturation of any of the formation fluid, oil, gas or water, is below a given value that fluid will not flow and only the other fluids can be produced from the formation. For example, in certain virgin oil reservoirs with low gas and water saturations, only oil, and not gas or water, will be produced. At the other extreme the formation may be watered out and have no free gas and, although the formation contains appreciable quantities of oil, no oil or gas can be produced; only water will flow.

While it is essential to the practice of this invention that there be a mobile fluid, it should be understood that it is not necessary that the other fluids be immobile. However, analysis of the results becomes more complex when two fluids or more are flowing. In such a case it may be necessary to employ reservoir modeling techniques together with the principles of chromatography to satisfactorily analyze the results. Where only minor quantities of one or two are being produced, the simplified approach of equation 1 is preferred. This method will be reasonably accurate so long as one of the fluids is at least 90 percent of the total volume produced. This approach can be further refined by estimating the average velocities of the tracers to account for flow of the "immobile" fluid. Hereinafter, the fluid with the highest saturation will be referred to as the mobile fluid and the fluids with the lower saturations will be referred to as the immobile fluids. This phraseology is employed for convenience and clarity and it should be understood that the immobile phases may, in fact, be capable of flow.

In the illustrative example, no free gas was present in the pore spaces of the formation. The presence of free gas, however, would not be detrimental to the practice of this invention. In fact, the gas saturation of the formation could also be determined by this method. However, it will be more convenient in many instances to determine the gas saturation by methods such as gas-liquid recombination and employ the method of this invention to determine the relative quantities of oil and water. When the method is used in such a manner, the tracers should have a low vapor pressure at reservoir temperature so that no appreciable amounts will be vaporized and go into the gaseous phase. Under these circumstances this method will determine the relative amounts of liquids, oil and water, in the formation and any free gas would not affect this result. It will, of course, be necessary to determine the pore volume of the reservoir and the amount of free gas saturation to determine absolute values for the quantity of oil and water present in the formation. The porosity and gas saturations can be determined using conventional reservoir analytical techniques such as core analysis and gas-liquid recombination methods.

The carrier fluid must be miscible with the mobile fluid and must be capable of solubilizing the tracers which it carries. Its solubility in the immobile fluids must be low enough that for practical purposes it can be considered insoluble in these fluids. The carrier fluid should be in the same state as the mobile fluid. It should be a gas where formation gas is the mobile fluid and a liquid where oil or water is the mobile fluid. For example, if the formation fluids in a virgin oil reservoir are to be measured where oil is mobile and gas and water are immobile, the carrier liquid might be lease crude oil. Where formation water is the mobile liquid, produced formation water may be conveniently employed as the carrier liquid. Where gas is the mobile fluid, natural gas may be used as the carrier fluid. As a practical matter, the mobile fluid, oil, gas or water, previously produced from the formation, is an excellent carrier fluid. In producing oil fields these fluids are readily available; since they are in fact the mobile fluid there is no question of miscibility with the mobile fluid in the formation.

The tracers, of course, must be soluble in the carrier fluid. Moreover, they must be sufficiently soluble that their concentrations in the injected carrier fluid will be at or above a minimum level. As a minimum, the concentrations of the tracers when injected should be great enough that their presence in carrier fluid can be detected at the other location in the formation. In determining the concentrations to be employed, the effects of dispersion and diffusion should be considered as well as the sensitivity of the detection means. Where the carrier fluid is gas, the tracers should be gaseous. Where the carrier fluid is a liquid, the tracers may be liquids, dissolved solids, dissolved gases or combinations. Tracers which will interact with or be adsorbed by the formation rock, or course, should not be employed in the practice of the method.
The partition coefficients which are used in the chromatographic analysis are ratios which describe the equilibrium distribution of a tracer between phases. These ratios are also known as distribution coefficients and equilibrium ratios and can be determined by simple experimental procedures. Where only two phases exist in the reservoir, as in the prior example, a two-phase partition coefficient is determined for each tracer. Known quantities of the carrier fluid, the immobile fluid, and the tracer are combined and vigorously agitated to insure complete and uniform mixing of the three components. After the system has reached equilibrium at reservoir conditions and the carrier and immobile fluids have segregated, the concentration of the tracer in each of the fluid phases is determined. The ratio of these concentrations is the partition coefficient for that tracer in that fluid system. A more detailed description of these partition coefficients is given in the cited article by Raimondi and Torcaso.

Where oil, gas and water coexist in the reservoir, three-phase partition coefficients must be determined if the method of this application is used to ascertain the relative saturations of all three fluids. Three-phase partition coefficients are determined in a manner similar to the two-phase partition coefficient except that a third fluid, the second immobile phase, is added to the system and the tracer concentration in the carrier fluid and each of the immobile fluids is established. Where the saturation of one of the three fluids is to be independently established and not by the method of this invention, the two-phase partition coefficients can be used so long as the tracers are essentially insoluble or will not vaporize to any appreciable degree in that fluid.

The tracers must have different partition coefficients between the carrier fluid and immobile phase or phases. Theoretically, any difference in partition coefficients would be satisfactory. As a practical matter, however, one partition coefficient should be at least twice as great as another to clearly distinguish the arrival of the tracers at the second location. Moreover, if the distance between injection and detection locations in the formation is relatively short, such as between two vertical points in the same formation, a radical difference in partition coefficients is preferred due to the short travel time for both tracers. The best results are obtained in such a case where one tracer is substantially insoluble in the immobile liquid and the second tracer is more highly soluble in the immobile liquid than in the carrier fluid. The partition coefficient for the first tracer would be infinite; for the second tracer it would be less than one.

Where the method is employed to determine connate water saturation where oil is the mobile fluid and brine is employed as the carrier liquid, a high molecular weight alcohol, such as normal pentanol, could be satisfactorily employed as tracer A and a low molecular weight alcohol, such as methanol, could be employed as tracer B. Both alcohols would be satisfactorily soluble in a carrier liquid, and their partition coefficients between the carrier liquid and formation water would be great enough to clearly distinguish their arrival times.

A minimum of two tracers are required in the practice of this invention. Two tracers can be used when only two fluids, oil-water or gas-water, exist in the reservoir or where three fluids are present and the saturation of one fluid is determined by independent means. However, even under these circumstances, more than two tracers may be employed. A third tracer with a partition coefficient which differs from those of the other tracers would give additional comparative information. A fourth would give even more information. There are, of course, limitations on the number of tracers that can be employed. One tracer may have an effect on solubility of another. Also there are economic limitations on the number of tracers to be employed.

The carrier fluid itself may serve as one of the two required tracers if it can be satisfactorily distinguished from the mobile phase which it displaces. For example, a formation might contain only immobile oil and mobile brine with a high chloride ion concentration. In determining the liquid saturations of this formation, fresh water containing an alcohol might be used. The alcohol would serve as one tracer. The fresh water would be the carrier liquid and would also be a tracer since it could be distinguished from the brine on the basis of the chloride ion concentration of the two liquids.

Where three fluids, oil, gas and water, are present in the formation and the saturation of each fluid is to be determined by this method, at least three tracers are required. For example, in a formation having water as an immobile phase and oil and gas as immobile phases, a carrier fluid of water containing sodium bromide, methanol and isobutyl alcohol could be employed. The three tracers are all soluble in water. The sodium bromide is essentially insoluble in the gas and oil. The methanol would be more soluble in the gas than the isobutyl alcohol due to its higher vapor pressure. The isobutyl alcohol has a lower vapor pressure and will be more soluble in the oil and less soluble in the gas. The analysis of the results is quite naturally more complex when three tracers are used to determine the saturations of three formation fluids. However one skilled in the art can readily determine these saturations by applying the principles of chromatography in accordance with the teaching of this application.

In the illustration the production and injection rates were equal and constant. It should be noted, however, that these conditions are not essentially characteristics for the practice of this invention. It is only necessary that the tracers traverse the same region of the reservoir. Any injection-production method which will satisfy this condition may be satisfactorily employed.

It should also be noted that it is not essential that the tracers be simultaneously injected into the reservoir. Simultaneous injection would be more convenient in most instances and, therefore, would be preferred. However so long as the tracers traverse the same region of the formation, they can be injected together or sequentially and the results analyzed accordingly. The produced fluids can be analyzed for the presence of the tracers in any convenient manner. Conventional chemical analytical techniques, such as qualitative-quantitative methods, conventional chromatographic methods and the like, can be employed. Also, it is contemplated that the tracers may be radioactive isotopes and that their arrival times may be determined with radiological means.

The technique of this invention is applicable to a between-wells process as described above or to a single-well process where the carrier fluid and tracers are injected at one location in a reservoir and withdrawn from a second, vertically spaced location in the reservoir at the same well. The single-well process may be carried out in a cased or uncased well. There the well is cased, the well casing would be perforated at two vertical locations within the reservoir. A well assembly including a straddle packer and a string of tubing would then be placed in the well casing. The tubing string would provide fluid communication between the surface and the lowermost set of perforations; the straddle packer would block fluid communication between the tubing casing annular spaces above and below the packer. The carrier fluid with tracers could then be injected into the formation through one set of perforations and withdrawn through the other. The tubing string would provide a flow conduit in one direction, the tubing-casing annular space would provide a flow conduit in the other direction. Where the well is uncased, the method would be carried out in a similar manner except that there would be no casing to be perforated.

The principle of the invention, a detailed description of one specific application of the principle, and the best mode in which it is contemplated to apply that principle have been described. It is to be understood that the foregoing is illustrative only and that other means and techniques can be employed without departing from the true scope of the invention defined in the following claims.

What I claim is:
A method for determining the relative amounts of two fluid phases in a subterranean reservoir formation wherein one of the phases is mobile and the other is essentially immobile comprising injecting into the formation at a first location a carrier fluid which is substantially insoluble in the immobile fluid phase and miscible with the mobile fluid phase, incorporating in the carrier fluid at least two tracers which have different partition coefficients between the carrier fluid and the immobile fluid phase, the concentration of each tracer being sufficient to enable its detection at a second location in the formation, displacing the carrier fluid and the tracers to the second location in detectable quantities, detecting the tracers at the second location and measuring at least one property related to the chromatographic behavior of each of said tracers to determine the relative amounts of the two fluid phases in the formation.

A method as defined by claim 1 wherein the carrier fluid is a liquid.

A method as defined by claim 2 wherein the carrier fluid is aqueous.

A method as defined by claim 2 wherein the carrier fluid is an oil.

A method as defined by claim 1 wherein the carrier fluid is gaseous.

A method as defined by claim 1 wherein the partition coefficient of one of the tracers is at least twice as great as the partition coefficient of another of the tracers.

A method as defined by claim 1 wherein the first location in the formation is at one location in a well and the second location in the formation is in the same well and is vertically spaced from the first location.

A method as defined by claim 1 wherein the first location in the formation is at one well and the second location in the formation is at a second well which is horizontally spaced from the first well.

A method for determining the relative amounts of two fluid phases in a subterranean reservoir formation wherein one of the phases is mobile and the other is essentially immobile comprising injecting into the formation at a first location a solution consisting of a carrier fluid which is substantially insoluble in the immobile fluid phase and which is miscible with the mobile fluid phase and a tracer which is soluble in both the carrier fluid and the immobile fluid phase, the quantities of the carrier fluid and the tracer being sufficiently great to enable detection at a second location in the formation, displacing the carrier fluid-tracer solution to the second location in detectable quantities, detecting the carrier fluid and the tracer at the second location and measuring at least one property related to the chromatographic behavior of the carrier fluid and the tracer to determine the relative amounts of the two fluid phases in the formation.

A method of determining the relative amounts of oil, gas, and water in a subterranean oil-bearing formation in which a first of the fluids is mobile and the second and the third fluids are essentially immobile which comprises injecting into the formation at a first location a carrier fluid which is substantially insoluble in the immobile second and third fluids and which is miscible with the mobile first fluid, incorporating in the carrier fluid at least three tracers having different three-phase partition coefficients between the carrier fluid and the immobile second fluid and between the carrier fluid and the immobile third fluid, the concentration of the tracers being sufficiently great to enable detection at a second location in the reservoir, displacing the carrier fluid and tracers to the second location in the formation detecting the tracers at the second location and measuring at least one property related to the chromatographic behavior of each of said tracers to determine the relative amounts of oil, gas, and water in the formation.