MASTER

DOE contract EW-78-C-19-0007 between DOE and Donald C. Bond covers "Study of the Potential for Future Work on Methods of Determining Residual Oil". Attached is a Progress Report for Phase I of this study, made in the period January 1 to April 30, 1978.

Donald C. Bond

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ABBREVIATIONS AND SYMBOLS

ROS	Residual Oil Saturation
TOR	Tertiary Oil Recovery
NML	Nuclear Magnetic Log
PNC	Pulsed Neutron Capture
R & D	Research and Development
IOCC	Interstate Oil Compact Commission
L-I-L	Log-Inject-Log
S_{or}	Symbol for Residual Oil Saturation Value
S_{oi}	Symbol for Initial Oil Saturation Value
ϕ	Symbol for Porosity

PROGRESS REPORT,

STUDY OF THE POTENTIAL FOR FUTURE WORK ON METHODS OF DETERMINING RESIDUAL OIL SATURATION,

(Phase I, January 1 to April 30, 1978)

Introduction

In the contract for this study we agreed that during Phase I I would consult with industry experts in the determination of residual oil saturation (ROS). In preparation for interviews with these experts, a list of questions for discussion was prepared (Appendix A, attached). Sources for the list were various publications about residual oil, especially (1) "How Should We Measure Residual Oil Saturation," by R. E. Wyman, Bull. Can. Petrol. Geol., vol. 25, No. 2 (May, 1977), p. 233-270; and (2) "Determination of Residual Oil Saturation," a book prepared by the Research Committee of the Interstate Oil Compact Commission, D. C. Bond, C. R. Hocott, and F. H. Poettmann, Editors, to be published in June, 1978.

In interviews with experts, these subjects were discussed: (a) the most pressing needs for research and development in methods of determination of residual oil saturation, (b) tools and techniques that need to be improved, and (c) possible new tools and techniques that are worthy of feasibility studies or development. In the interviews little time was spent on R & D that is being done by industry: oil companies, service companies, and suppliers. Also, little time was spent on R & D that is likely to be done by industry in the future. The problems that were emphasized were those that are not likely to be handled by industry in the normal course of events—worthy projects that probably will not be undertaken without support from DOE.

In subsequent discussions with people in oil companies and service companies the list of questions was expanded, as new ideas were brought out. A copy of the expanded list, containing about 50 questions, is attached as Appendix

A of this report. This expanded list will be the basis for future discussions, in Phase II of the DOE project.

In the period January 1 to April 30, 1978, five oil companies, two service companies, and two universities were visited. Thirty persons were interviewed. In some cases it was necessary to contact, by phone or letter, people who had been interviewed, in order to expand or clarify points that had been discussed in the interviews.

In order to consider future research that may be needed on ROS, we should have some understanding of the state-of-the-art of determining ROS. The Wyman and IOCC references, cited above, describe present methods in detail, so a complete description of these methods need not be given here. Appendix B of the present report is a brief summary of the state-of-the-art of determining ROS. This summary gives the background for discussion of various possibilities for research related to methods for determining residual oil saturation.

Results of Interviews and Tentative Conclusions in Phase I

In Phase I of this project (January 1 to April 30, 1978) 30 persons were interviewed in five oil companies, two service companies, and two universities. In four cases the companies preferred that research personnel handle the questions, while in the other three cases they preferred that operating people be consulted.

Considerable difference of opinion was found with respect to any given potential research project:

- the need for the project
- the feasibility of accomplishing what was desired
- the priority that should be assigned to the project
- whether DOE should fund the research and, if so, the amount of support that was warranted.

Because of this difference of opinion, it would be premature to make judgments and firm recommendations with respect to an R & D program for DOE until the rest of the interviews have been completed, in Phase II of this study

(May 1 to August 31, 1978). However, at this stage research support does appear to be needed in these areas:

Log calibration and testing facilities

Precision of PNC and other logging tools

Measurement of neutron capture cross section of cores

Measurement of neutron capture cross section of pure elements

L-I-L in water-saturated rocks

New, or improved, core barrels with:

- near-zero mud filtrate flushing
- better pressure retention
- higher pressure and temperature limits

Single-well tracer method:

- results in stratified reservoirs
- determination of S_{or} in gas cap
- sensitivity of derived value of S_{or} to various parameters
- errors in S_{or} caused by difference between the compositions of trapped oil (behind the flood front) and produced oil—effect on distribution coefficient of tracer

Log-inject-log with untested combinations:

- gamma-ray log with radioactive water
- resistivity log with waters having contrasting salinity

Factors that may cause errors in values of S_{or} determined by means of shallow investigation tools:

- displacement of residual oil when capillary number is exceeded
- end effects and capillary imbibition
- invasion by drilling mud particles

Application of complete suite of methods for determination of ROS, in TOR projects that have DOE support

Material balance studies to determine S_{or} , with attention to the conversion of data to true reservoir conditions

Application of statistics (experiment design) in the planning of a program of coring, logging, etc. that will maximize the quality and the amount of information about S_{or} , for minimum cost

Estimation of S_{or} from the velocity of a micellar flood front, in a mini-test

Survey of Russian literature on ROS determination

Seminar on ROS determination

Among those who think that research in the above areas is needed, not everyone agrees that this research should be funded by DOE. Of course, in Phase II of this study our opinions about the above projects could be modified and other worthwhile projects could be added to the list.

For about two-thirds of the potential projects listed above, the recommended amount of funding probably will be in the range of \$100,000 to several hundred thousand dollars each. Funding for a few small projects could be in the range of ten to fifty thousand dollars each. If all of the projects were undertaken, the cost would probably be on the order of \$2,500,000. Of course, these are tentative conclusions that are subject to revision as the study proceeds.

Phase II

In Phase II of this project (May 1 to August 31, 1978) people in 4 or 5 other oil companies and one other service company will be interviewed. Several engineering design companies will be contacted by phone or letter, or perhaps will be visited. Questionnaires will be sent to a few individuals who have been active in the area of ROS determination; visits will be arranged where warranted.

Phase III

In Phase III (September 1 to December 31, 1978) a selected list of potential R and D projects will be prepared. This list will be sent to the people who have been contacted during Phase I and Phase II. Opinions of these people will be solicited concerning the need, feasibility, priority, DOE support and amount recommended—for each of the potential projects.

Finally, a judgment will be made about the various projects. A recommended R and D program on ROS determination will be prepared and submitted to DOE.

APPENDIX A

QUESTIONS FOR DISCUSSION—R & D NEEDS IN DETERMINATION
OF RESIDUAL OIL SATURATION

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Logging, Miscellaneous

What is the depth of investigation of various tools and methods used in the determination of ROS?

Should improved casing materials be developed that will permit better resistivity logging in cased holes?

Should an NML tool be developed that will go into small holes (<7 inches diameter)? Is this feasible?

Can a Nuclear Magnetism Log be developed that will investigate as deeply into the reservoir as the Resistivity Logs?

Will industry develop NML logging devices with higher signal/noise ratio?

Can a reliable, stable carbon/oxygen log be developed that will give S_{or} with sufficient accuracy for TOR evaluations?

Dielectric Constant Logging—can we refine this to permit estimation of residual oil content?

Can a down-hole gravimeter be perfected that will give S_{or} with sufficient accuracy for use in evaluation of TOR applications?

Should we investigate the effects of the following on ROS values that result from use of shallow investigation tools: (a) Displacement of residual oil when critical capillary number is exceeded? (b) End effects and capillary imbibition? (c) Invasion of rock by drilling mud particles?

Log-Inject-Log

What about the log-inject-log method with chemical stripping of the oil? Is this an area that DOE should support?

Log-inject-log techniques might be developed using radioactive water and gamma-ray logs (described by Wyman, "How Should We Measure Residual Oil Saturation," Bull. Can. Petrol. Geol. Vol. 25, No. 2 (May, 1977), p. 233-270). We might inject radioactive water before and after removal of residual oil, thus eliminating need to know porosity. Should DOE support this work?

What other log-inject-log procedures merit development?

Logging, PNC

Should an installation be set up containing rocks of different porosities, and different lithologies, with accurately known fluid saturations, for testing and calibrating various tools (PNC, C/O, NML, etc.). For example, rocks containing (a) 100% oil, (b) oil with connate water, (c) residual oil, and (d) 100% water?

What is the degree of precision of available PNC equipment? What precision is potentially feasible?

Can a routine method be developed for the determination of the neutron capture cross-section of cores of various sizes?

Is industry developing adequate charts (departure curves) for correcting for diffusion effects in PNC logging?

Are departure curves needed for the PNC log, to correct for the effects of bore-hole size, casing configuration, porosity, and salinity?

Is field research warranted on log-inject-log methods in water-saturated rocks? For example, effect of kind of completion (cased, uncased, casing centered and not centered), effect of porosity, effect of salinity (fresh water, 50,000, 100,000 p.p.m. TDS, etc.), effect of heterogeneity of reservoir rock?

Could the results of the above study tell the degree of flushing during ROS determination by the log-inject-log technique?

Should the neutron capture cross-section of pure elements (Si, Ca, and other elements found in reservoir rock) be measured accurately, to improve on interpretation of PNC logs?

Coring and Core Analysis

What are the chances of developing a practical core barrel with zero flushing of cores by mud filtrate? (See Maurer Engrg. Rpt., etc.)

What are the chances of combining such a core barrel with pressure coring to give essentially unflushed cores under in situ conditions? Are these projects that DOE should support?

Would there be merit in a coring device that would trap all fluids in the cored interval, after the reservoir pressure was released? Feasibility? DOE support?

Is an improved pressure coring device needed to core in deeper wells (higher temperature and pressure)? (For example, for evaluation of potential high-pressure CO₂ floods.) DOE support?

Should more work be done on the effect of reservoir temperature and pressure (vs. ambient temperature and pressure) on porosity and formation resistivity factor of cores? Can better rules-of-thumb be developed for taking into account the effects of temperature and pressure, permitting use of results obtained under ambient conditions? Is this an area for DOE support?

More work may be needed on the determination of the factor to be used in converting from $(\bar{S}_o)_{\text{core}}$ to $(S_o)_{\text{res}}$ —in order to develop better rules-of-thumb to correct for the effects of flushing by mud filtrate and expulsion by gas evolution?

Should laboratory determinations of S_{or} be done on (a) restored-state cores or (b) fresh, native-state cores? Is more work needed in this area?

Can oil saturations deduced from cores be used to deduce gradients in saturation over the reservoir, even though uncertainty exists about the absolute value of the oil saturation?

Tracer Methods

In tracer methods we need to know how stratification of the reservoir rock affects the results. The tracer method yields S_{or} that usually is less than the average S_{or} determination by other methods. Why?

Is research needed on the application of the single-well tracer method in the determination of ROS in a gas cap?

Can the single-well tracer method be used to determine reservoir relative permeability in situ?

What about computer studies (in single-well tracer determinations of ROS) on the sensitivity of the ROS value to changes in various parameters?

Core Laboratories, Inc. formerly offered, as a service, the running of single-well tracer tests for determination of ROS. Should DOE help to set up a not-for-profit service of this kind (for example, at Rice University)? (This service may be offered by Dowdco?)

Would it be worthwhile to run some single-well tracer tests on fractured wells (before and after fracturing)?

Miscellaneous

Should DOE require a complete suite of S_{or} determinations (logging, coring, log-inject-log, tracer, material balance, etc.) on every DOE field test of an enhanced oil recovery process?

Should DOE support other studies involving complete suites of S_{or} determinations, in other reservoirs that may or may not be candidates for TOR?

How can we explain results of Murphy et al. (SPE 5804, 1976 Symposium on Improved Oil Recovery) "contrary to expectations, high residual oil saturations were measured in some high permeability intervals."? Should this Murphy et al. anomaly be studied?

Conceivably a TOR process, using viscous polymer chaser, could have a higher pattern efficiency than a prior waterflood. Thus, we may need to know the S_{or} even in parts of the reservoir that are not contacted by flood-water. How much of the reservoir is likely to be affected by such a TOR process? How can we determine the S_{or} in the part affected by such a TOR process, but not by waterflood?

How much of the oil that is by-passed by the tracer fluid will a TOR fluid contact if the mobility ratio of the TOR fluid, with respect to the reservoir fluid, is favorable?

Should more material-balance studies be made, using core data taken under true reservoir conditions, to obtain better estimates of original oil in place—which might lead to better estimates of residual oil after waterflooding, in turn give rules-of-thumb for estimation of S_{or} in potential TOR projects?

Should DOE support these studies?

Miscellaneous (Continued)

How about a small feasibility study concerning the determination of ROS by seismic methods (well-to-well, etc.)?

Should more work be done on the estimation of S_{or} from total compressibility of reservoir rock and fluids, as calculated from the results of interference tests?

Can we use statistics (design of experiments) to design the program of coring, logging, etc. that will give the most ROS information for the least expenditure of money?

Is research needed on methods of determining oil saturation in unconsolidated sands containing heavy oil, at high temperature (for steam floods)? Doe support?

Does Russian literature merit a literature search (sponsored by DOE) with respect to methods of determination of residual oil saturation? Is a "State-of-the-Art" report on Russian work on ROS determination warranted?

Should we organize a seminar ($\pm$ one week), similar to Gordon Research Conference, limited to 40-60 experts, to study intensively methods of determination of ROS and attempt to develop new concepts and new approaches?

APPENDIX B

BRIEF SUMMARY OF THE STATE-OF-THE-ART WITH RESPECT TO METHODS
OF DETERMINATION OF RESIDUAL OIL SATURATION

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Why Do We Want to Know the Residual Oil Saturation in a Reservoir?

When we are evaluating the tertiary oil recovery (TOR) potential of a waterflooded reservoir, we would like to know the total amount of oil remaining in the reservoir and we would like to know how this oil is distributed. Especially we would like to know the amount of oil, the oil saturation, and the spatial distribution of the oil in the part of the reservoir that has been subjected to waterflood—the part of the reservoir that is likely to be affected by injected fluids in a TOR process.

In some cases (100% water-wet, homogeneous reservoirs) the oil saturation in the waterflooded part of the reservoir can be expected to equal the theoretical saturation that is attained in laboratory tests on cores. These tests may be waterfloods on preserved or reconstituted cores, relative permeability tests, or capillary imbibition tests. In other cases (oil-wet or partially oil-wet reservoirs) the theoretical residual oil saturation may not have a unique value. In any case, what we want to know is the oil saturation—and its distribution—in the waterflooded portion of the reservoir. We want this information to enable us to estimate the amount of oil that is potentially recoverable in a TOR process.

We use the term "Residual Oil Saturation" here because we do not have a short-hand way of saying: "Oil Saturation in that Part of the Reservoir that Has Been Subjected to the Passage of the Waterflood Front and is Likely to be Subjected to the Effects of Injected Fluids in a TOR Process."

We need to keep in mind the likely possibility that S_{or} will vary within the waterflooded reservoir. Variations in S_{or} can be caused by pattern effects, heterogeneity of rock, especially stratification, and wettability-relative permeability effects. After water breakthrough occurs in a flood,

the flood pattern expands in a direction approximately perpendicular to the flow lines. Because the region near the edge of the pattern is subjected to the action of smaller volumes of floodwater than the region swept by the main part of the flood, a gradient in S_{or} exists in the outer part of the pattern, perpendicular to the direction of flow. Stratification of the reservoir rock leads to variations in S_{or} that are well known and need not be discussed here. (The problem of heterogeneity in reservoirs is treated in a book: "Modern Reservoir Description for Improved Oil Recovery," now being prepared by the Research Committee of the Interstate Oil Compact Commission.) In reservoir rock that is not 100 percent water-wet, S_{or} can vary substantially with the number of pore volumes of floodwater that have flowed through a given part of the reservoir; thus, a gradient in S_{or} can be expected along the direction of flow.

These variations in S_{or} —variations caused by pattern effects, stratification, and wettability—are difficult to measure. But they should be kept in mind in any evaluation of a TOR prospect.

List of Methods Currently Used for the Determination of Residual Oil Saturation

Residual oil saturation is determined by use of the following techniques or tools:

- Material balance method
- Analysis of cores (conventional or pressure core barrel)
- Laboratory tests on preserved or reconstituted cores
- Single-well tracer method
- Logging tools
 - Resistivity
 - Pulsed Neutron Capture (PNC)
 - Nuclear Magnetism (NML)
- Log-inject-log methods that employ these tools, especially the PNC log

In addition to the above, certain techniques and tools have been proposed or are currently being developed and tested:

- Resistivity log-inject-log
- Gamma radiation log-inject-log
- Dielectric constant log
- Carbon/oxygen log

Radius of Investigation of Methods for the Determination of ROS

In a general way we can classify methods of determining ROS according to the amount of the reservoir that is sampled, or the radius of investigation of the tool that is used.

The material-balance method gives information about the entire reservoir. The single-well tracer method usually tells something about an average sample out to a distance of 10 to 20 feet from the well; the radius of investigation is limited only by the volume of tracer fluid that can be economically injected. Certain logs (laterolog, induction log, PNC log) sense the physical properties of the rock out to a radius of several inches to perhaps two feet. Other logs (NML, dielectric constant log) have shallow depth of investigation (1 to 2 inches). Finally, cores give a sample of the actual reservoir itself; the problem, of course, is to take this sample without changing it in the process of coring.

Advantages, Disadvantages, and Limitations of Various Methods for Determining Residual Oil Saturation

Each method for determining ROS has certain advantages and disadvantages. No single method is the best one to use universally. The applicability of each is limited, depending upon the nature of the reservoir, the kinds of wells available, and other factors. Following is a brief discussion of the advantages, disadvantages, and limitations of methods for the determination of ROS. For more detailed descriptions the reader is referred to the Wyman and IOCC references mentioned above (page 1 of this report).

Material Balance Method

In this method the amount of oil produced by primary production and by conventional secondary recovery is subtracted from the estimated initial oil-in-place in the reservoir, at the time of the discovery of the reservoir. The initial oil-in-place is calculated by means of the equation:

$$\text{Initial Oil-in-Place} = N = Ah\phi S_{oi}/B_i$$

Where A = area
 h = thickness of pay zone
 ϕ = porosity
 S_{oi} = initial oil saturation
 B_i = initial formation volume factor

The weakness of the material balance method lies in the great uncertainty about the value of N . The area A is seldom known accurately. Sometimes not all of the oil-saturated rock is considered to be productive; the thickness of oil-producing rock, h , is often, at best, an estimate.

The porosity of the reservoir rock can be determined from cores. However, in a heterogeneous reservoir it may be very difficult to obtain cores that give a representative sampling of the whole reservoir. There is always the problem of trying to determine the porosity under reservoir conditions—especially under reservoir pressure. Porosity can be estimated from various logs (neutron, density, sonic); however, it is not easy to determine porosity in this manner with the accuracy required for ROS determination in TOR evaluations.

Probably the best way to determine S_{oi} is to core with lease oil, determine S_{wi} (initial water saturation) in the cores, and calculate S_{oi} from the equation: $S_{oi} = (1 - S_{wi})$. But many operators are reluctant to core with crude oil. Furthermore, where a transition zone exists between the oil and water sands, mobile water can be displaced during coring; incorrect values of S_{oi} are obtained, greater than the true values.

Of course, S_{oi} can be estimated by means of conventional resistivity log interpretation, using the classic Archie Treatment: $S_w = \left(\frac{R_w \phi^{-m}}{R_t} \right)^{1/n}$. But this treatment requires that formation-water resistivity— R_w , porosity— ϕ , lithology exponent— m , and saturation exponent— n all be known accurately for the particular zones that are being studied. Furthermore, the quantities ϕ , m , and n must be evaluated under reservoir conditions.

Uncertainties about the parameters A , h , ϕ , and S_{oi} lead to a corresponding uncertainty about the values of N and S_{or} . Therefore, S_{or} seldom can be evaluated by the material balance method with sufficient accuracy for TOR evaluation. However, the material balance values of S_{or} can be useful. For example, if the material balance value of S_{or} is twice the value of S_{or} obtained by other methods, perhaps substantial areas exist in the reservoir where infill drilling would be profitable.

Analysis of Cores—Laboratory Tests on Cores

Conventional cores. In general, fluid saturations in conventionally cored rock are subject to change, either during the process of coring or as the cores are raised to the surface. Any mobile oil that is present in the reservoir rock will be flushed from the cores by mud filtrate, to some degree. Even though the oil content of the rock is not mobile with respect to the normal pressure gradients that exist during waterflooding, some of the residual oil can be flushed out by mud filtrate because of the abnormally high gradient that can exist across the rock that is being cored. Of course, evolution of dissolved gas, as the core is brought to the surface, can cause the expulsion of some oil and water from the core.

If the reservoir contains no mobile oil and if the residual oil contains a negligible amount of dissolved gas, under low pressure, cores, properly taken, may have oil saturations that are not greatly different from the oil saturation in the reservoir. We can be confident that the oil saturation in the reservoir is at least as great as the saturation found in the cores.

Attempts have been made, in the laboratory, to reproduce the processes that occur during coring and to deduce corrections for the effects of mud filtrate flushing and gas expulsion. In some special cases these corrections appear to lead to fairly accurate values of S_{or} . But, as Wyman puts it (reference cited

above, page 1 of this report), " . . . we are still far from being able to make reliable corrections to account for flushing and blowdown in conventional cores."

Pressure corings. The pressure core barrel enables one to cut and recover cores without the evolution of gas that occurs during conventional coring. Thus, the loss of oil caused by expulsion of gas, as well as the shrinkage of the oil in the core, is prevented (Hagedorn, A. R. and Blackwell, R. J.: "Summary of Experience with Pressure Coring," SPE Paper 3962 presented at 47th Annual Fall Mtg. of SPE-AIME, Oct. 8-11, 1972, San Antonio, Texas).

The pressure core barrel itself does not prevent flushing of the core by mud filtrate. Generally, in pressure coring, attempts are made to minimize flushing by using mud that has: low weight; no surface-active chemicals; low spurt loss and low water loss; particulates sized for the formation being cored; and a tracer, such as tritium, for monitoring filtrate invasion. At the surface the core is frozen so that it can be transported to the laboratory for analysis.

Under ideal conditions pressure coring is one of the best ways to obtain S_{or} . Of course, as with conventional coring, a new hole is required and no mobile oil should be present in the cored interval. (Under unusual conditions the drilling of a new hole may be avoided; for example, sometimes it is possible to deepen a shallow hole into part of the reservoir that has been flooded by natural water drive.)

We have no absolute standard with which values of S_{or} determined by various methods can be compared. We can only compare the values of S_{or} with what appear to be the best values, as determined by other methods. In one study involving five determinations good agreement was obtained between S_{or} as determined by pressure coring and the best estimate of S_{or} by other methods. In the IOCC book mentioned above (page 1) a similar comparison for about twenty determinations showed fair agreement in about two-thirds of the cases.

Although the pressure core barrel gives reliable estimates of S_{or} under ideal conditions, these ideal conditions are difficult to obtain. One company reports poor results in about 50 percent of its pressure coring, due to partial loss of pressure and other factors. Another company reports "great difficulty" in obtaining satisfactory pressure cores. In part, the problem appears to lie in the fact that not enough pressure coring has been done to make it worthwhile for the service company to maintain a trained, experienced stand-by crew available at all times. Also, maintenance of the equipment may suffer when the core barrel is used on an intermittent basis. Anyone who contemplates use of the pressure core barrel should investigate these problems. Recently considerable improvement in the available service for pressure coring has been claimed, as a larger volume of business has been generated.

Laboratory Tests on Cores

In the laboratory various special tests are used to obtain an estimate of the value of S_{or} that is to be expected in the flooded part of a reservoir. The cores that are studied may be cores that are preserved, as taken from the core barrel, or they may be reconstituted cores, where an attempt is made to duplicate reservoir conditions. The principal tests involve waterfloods, relative permeability measurements, imbibition measurements, and centrifuge experiments. Preferably these tests are made under reservoir conditions, with reservoir oil and the interstitial water that is present in the reservoir.

The estimation of S_{or} by these methods is an art in itself. As with other methods, we are handicapped by lack of knowledge of an absolute standard of comparison. There is some evidence that in water-wet cores reliable estimates of S_{or} can be obtained by waterflood or imbibition experiments. In oil-wet rocks, or rocks of intermediate wettability, we may sometimes obtain fairly reliable values of S_{or} if proper precautions are taken. But in such rocks we always have two problems:

- (1) we can never be certain that we have duplicated the capillary fluid distribution that exists in the reservoir, and
- (2) the oil saturation is likely to be a function of the volume of flood water, so that a unique value of S_{or} does not exist. In reservoirs that contain such rocks the oil saturation behind the flood front is likely to exhibit a gradient, further complicating the estimation of the amount of oil susceptible to injection of TOR fluids.

Experts in this field of investigation agree that further research is needed. In particular, more studies should be made in which S_{or} as determined by these methods is compared with the best estimates of S_{or} by other methods. But, if the results are to be meaningful, these studies must be done by those who are highly skilled in the art of running tests of this kind.

Single-Well Tracer Method

The single-well tracer method makes use of a hydrolyzable tracer, such as ethyl acetate. This tracer is dissolved in formation brine, which is injected into a well to fill the reservoir pore space (minus the space occupied by residual oil, of course) out to a radius of about 10 to 20 feet from the well. Some of the primary tracer, ethyl acetate, hydrolyzes in the reservoir to form a secondary tracer, ethyl alcohol. The ethyl alcohol dissolves mostly in the brine, but the ethyl acetate is soluble in both brine and oil, distributing itself between brine and oil according to its partition coefficient between these two fluids.

When the well is back-flowed, the ethyl acetate and alcohol move at different rates. Analysis of the produced fluids, versus time, gives S_{or} by means of a curve-fitting technique. Curves for various assumed values of S_{or} are calculated by means of a computer program based upon the partition coefficient and chromatographic theory.

Certain precautions must be taken. The partition coefficient that is used must be the coefficient for the distribution of the primary tracer between the formation brine and the residual oil actually left behind the flood front in the reservoir. The composition of this residual oil is not necessarily the same as that of the produced crude oil. Further, the partition coefficient should be determined under reservoir temperature and pressure. Large volumes of pre-flush brine-tracer solution should be avoided, in order to keep from dissolving light ends from the residual oil and thus changing the partition coefficient. Finally, of course, a new well is preferable.

The main advantage of the tracer method is that it gives information about the oil saturation in a large volume of the reservoir. Thus, some of the problems with shallow-investigation tools (over-flushing, capillary end effects) are minimized. Also, the method can be used in either cased or open holes. The method gives a single value of S_{or} , rather than a saturation profile with depth. This single value is considered to be weighted in favor of the more permeable zones in the reservoir. Such a weighted average may or may not be advantageous in TOR evaluations; more study is needed about this question.

In the IOCC study cited above, comparisons were made between S_{or} determined by the tracer method and by other methods, for 14 wells. In all cases except one the tracer gave values of S_{or} about equal to, or less than, the value that was obtained by other methods. Apparently we can be fairly confident that the oil saturation in the reservoir is at least as great as that given by the tracer method.

Certain major oil companies are licensed by the patent holder (Exxon) and have acquired the know-how required to use the tracer method. These companies also have the equipment and the trained personnel to do the extensive analytical and computer work that is required in the application of the method. Formerly this kind of work was done by a service company that was licensed for

that purpose; it is understood that this company no longer offers this service. Probably any company that undertakes the use of the tracer method will need to develop its own capabilities with respect to chemical analyses and computer calculations, for the time being at least.

Logging

When we estimate the oil saturation in a reservoir by means of a single conventional geophysical log, we need to know certain physical properties of the reservoir rock and the reservoir fluids. For example, in order to calculate S_{or} from a resistivity log we need to know: the porosity of the rock, its cementation (lithology) exponent and saturation exponent, the clay content of the rock and the clay conductance, and the resistivity of the interstitial water in the rock. In general, we do not know the values of these parameters with sufficient accuracy to yield accurate values of S_{oi} ; an error of 5 to 10 saturation percent or more can be expected. In a virgin reservoir, where we want to know whether or not to complete a well, such an error is tolerable. But for TOR evaluation of a waterflooded reservoir we would like to know S_{or} with an accuracy of about 2 to 5 percent, so a single log may not yield satisfactory saturation values.

In some reservoirs it may be possible to compare log-derived values of S_{oi} with values of S_{oi} that have been determined by core analysis or other methods. In effect, through this comparison the logs are calibrated and the uncertainties due to errors in the values of the physical parameters are minimized. But in general we need better methods of determining S_{oi} from geophysical logs. The various log-inject-log procedures fill this need.

Log-Inject-Log Methods

In these methods a log is run in a well, fluid of one kind or another is injected into the reservoir, and the same log is run again. About ten different types of log-inject-log (L-I-L) techniques have been used or proposed.

The principal ones are based on the use of resistivity, pulsed neutron capture (PNC), or nuclear magnetism (NML) logs.

Resistivity L-I-L. In this method first the desired resistivity tool is run in the hole to give R_t , the resistivity of the reservoir rock, containing interstitial water plus residual oil at saturation S_{or} . Next, a solvent, mutually soluble in oil and water is injected into the reservoir to remove the residual oil. This solvent is displaced by water having the same composition as the original interstitial water. Finally, the same resistivity tool is run again to give R_o , the resistivity of the reservoir rock saturated with interstitial water. The residual oil saturation, S_{or} , is calculated from:

$$S_{or} = 1 - (R_o/R_t)^{1/n}$$

Of course, the saturation exponent, n , must be known, from imbibition experiments or other sources. The procedure does eliminate the need to know the porosity and the lithology exponent.

This method should measure whatever oil is present, whether it is mobile or immobile. It has the additional advantage that a deep investigating tool can be used, along with deep injection of solvent; thus, a larger, more representative fraction of the reservoir can be examined than with some of the other logging methods.

So far as is known, the resistivity L-I-L method has not been tested in the field.

Pulsed Neutron Capture L-I-L

The pulsed neutron capture (PNC) tool has a neutron generator which emits pulses of high-energy neutrons. In the rock around the bore-hole these neutrons lose energy until they arrive at the thermal state. The thermal neutrons are captured by nuclei of various atoms in the reservoir. Gamma rays

are emitted as capture occurs. Measurement of these gamma rays by the logging tool, at various times after the pulse, gives a means of measuring the capture cross section of the various nuclei in the reservoir.

The measured capture cross section is the sum of the cross sections of the rock matrix and of the fluids (water and hydrocarbons) within the pores. The capture cross sections of the fluids can be estimated from laboratory analyses and published correlations. Or, preferably, the cross sections of the fluids themselves are measured in special cells or tanks. The cross section of the rock matrix is estimated from the lithology of the rock or from experience in the area. (In some cases the capture cross section of the rock matrix has been determined from cores; large amounts of core material are required. Thus far, this procedure has not proved very practical.)

In the log-inject-log procedure that is most often used a PNC log is first run, with formation water and residual oil in the pores of the rock. Water is injected whose salinity differs as much as possible from the salinity of the formation water. The PNC log is then run again.

This procedure eliminates the need to know the capture cross section of the rock matrix. Simultaneous equations can be formulated which permit the calculation of S_{or} from the capture cross sections of the two waters and the cross sections that are measured by the two PNC logs. The calculation requires knowledge of the porosity, which is obtained from cores or logs.

In the PNC L-I-L procedure best results are obtained when the contrast between the salinity of initial and injected waters is at a maximum. As with other methods, injection rates should be low enough to avoid displacement of oil by viscous forces. The volume of injected water should be kept as low as possible, to minimize solution of light ends from the residual oil. Of course, no surfactants should be injected which might change the oil saturation in the reservoir.

In the PNC L-I-L procedure the assumption is made that all of the water that is initially present in the vicinity of the well-bore is displaced by the injected brine. Recent results from L-I-L tests on a cased hole in a water sand, reported by Exxon, cast grave doubt on this assumption (J. R. Bragg et al., "A Comparison of Several Techniques for Measuring Residual Oil Saturation," SPE Paper 7074, SPE Symposium on Improved Oil Recovery, April 16-19, 1978, Tulsa, Oklahoma, p. 375-388).

Other variations of the PNC L-I-L procedure have been used or proposed: (a) log-inject-log with alcohol strip, (b) log-inject-log with chlorinated hydrocarbon strip; and (c) log-inject-log with water having capture cross section adjusted to equal that of the residual oil. Each of these variations has certain advantages which are described by Wyman in the reference cited above (page 1). For example, with proper procedures the need to measure water capture cross sections and porosity can be eliminated.

The PNC L-I-L procedure can be run in open or cased hole. The effects of borehole, casing and cement are minimized or eliminated by the use of two successive logs.

In the IOCC study cited above, comparisons were made between S_{or} from the PNC L-I-L and from other methods. In most cases S_{or} as derived by the PNC method was at least as large as S_{or} from other methods. In about one-third of the cases the PNC value of S_{or} was significantly greater than the value given by other methods. Perhaps the PNC method is able to "see" oil saturation that is not measured by some of the other methods. On the other hand, perhaps some of the initial water is not displaced by the injected water, so that an erroneously high oil saturation is derived from the results of the test. This question needs to be investigated thoroughly.

Nuclear Magnetism-Inject-Log

In logging with the nuclear magnetism (NML) tool, a strong magnetic field is imposed on the fluid in the pores of the rock by sending a current through a coil in the bore-hole. The magnetization in the fluids approaches an equilibrium value that depends on the strength of the applied field. When the field is removed, protons in the fluids precess about the earth's magnetic field, causing an oscillating, exponentially-decaying voltage which is measured by the tool. For a given induced magnetization the magnitude of the signal depends on the total amount of hydrogen present.

In order to blank out signals from the mud in the hole, magnetite or other ferromagnetic particles are added to the mud. The measure of oil alone in the pores of the rock is accomplished by injecting into the reservoir an aqueous solution containing paramagnetic ions; these ions deaden any signal from the water phase. Thus, the signal is a measure of the bulk oil-in-place ($S_{or} \cdot \phi$). The value of ϕ from cores or logs is used to calculate S_{or} .

The NML inject-log procedure probably is the most accurate one available for the determination of S_{or} . Unfortunately it cannot be run in a cased hole. A relatively large hole (7 inches diameter) is required.

The NML tool which has been in use has relatively low signal-to-noise ratio. A new tool has been developed by Schlumberger which appears to give greatly reduced noise, resulting in greater signal-to-noise ratio. However, the stability of this new tool needs to be tested. Also, some experts have said that the validity of S_{or} values derived in L-I-L procedures with this tool needs to be thoroughly evaluated and verified, as was done with the other tool.

Other Possible Logging Techniques

Carbon/Oxygen Log

The Carbon/Oxygen log utilizes a pulsed 14 MeV neutron source and a gamma-ray detector. The tool is optimized for the production of "prompt" gamma

rays caused by inelastic scattering of neutrons by carbon. Although the present tool responds to large differences in oil saturation, it is not accurate enough to give S_{or} for TOR evaluation. There is optimism in some quarters about the possibility of eventually developing a satisfactory tool for S_{or} determination.

Dielectric Constant Log

Schlumberger has a new dielectric constant logging tool which is claimed to be the best tool available for the determination of S_{or} in open hole. Uncertainties caused by salinity changes are minimized or eliminated. The tool has shallow depth of investigation—about one inch. It is said to be much more stable than the NML tool. It has the further advantage of giving vertical resolution within about 2 inches. The tool needs to be thoroughly tested before judgment is passed on its merits.

Summary—Logging

When logs are used to estimate residual oil saturation for TOR evaluation, some kind of log-inject-log (L-I-L) procedure is required. In open hole best results have been obtained with the nuclear magnetism log (NML). The NML has the disadvantage of being a shallow investigating tool. An L-I-L procedure employing a resistivity tool could give a deeper radius of investigation. In cased hole the L-I-L procedure with the PNC tool is preferred. However, further work is needed to establish the validity of the assumptions made in this procedure; in particular, tests are needed in water-saturated sands.

In all types of L-I-L procedure the rate of injection must be kept low, so that the critical value of the capillary number is not exceeded during the injection phase of the test, causing the displacement of some of the residual oil. That is, the ratio of viscous to capillary forces must be kept as low as possible (J. J. Stosur and J. J. Taber, "Critical Displacement Ratio and Its Effect on Wellbore Measurement of Residual Oil Saturation," J. Petr. Tech. 28,

865-868 (Aug. 1976)). This precaution is especially important where tools with shallow radius of investigation are used. Further, procedures that employ these tools are susceptible to errors that are caused by: (1) invasion of the reservoir rock by mud particles, and (2) end effects caused by capillary imbibition. Research is needed to obtain quantitative estimates of all of these errors that may occur when shallow investigation tools are used.

Of course, in any L-I-L procedure no surfactant should be injected. Drift, caused by pressure gradients within the reservoir, should be counteracted by the injection of sufficient water. But the volume of injected water should be kept as low as possible.

CONCLUSIONS

STATE-OF-THE-ART OF DETERMINING ROS

Following is a brief digest of the methods that are preferred by many of the people who have worked on the problem of determining residual oil saturation.

Some operators have the opinion that one or more pressure cores should always be taken in any reservoir that is being evaluated for TOR. Other operators do not take such cores, because they consider the cost of pressure coring to be excessive, in view of uncertainties about core recovery and the results obtained from the cores.

The logging procedures that are preferred are the NML inject-log (in open-hole completions) and the PNC log-inject-log (in cased holes).

Single-well tracer tests often are run as a check on the results of pressure coring and log-inject-log tests. The tracer results probably are weighted toward the residual oil saturations that exist in the more permeable parts of the reservoir.

Other sources of information are used, to the extent that they are available, to supplement the results of the procedures described above. These supplemental sources include data from: material balance calculations, production tests and pressure-transient tests, conventional core analyses and log analyses, and injection profiles. In obtaining these supplemental data certain laboratory work may be involved; the laboratory data should always be converted to reservoir conditions, where this is possible.

The reader should be aware that the technology of ROS determination is in a fluid state. Old tools are being improved. New tools are being developed and tested. The availability of tools and services changes almost from month to month. Anyone who is considering the determination of ROS for the evaluation of TOR prospects should be alert for improvements that may be made in the art of making such determinations.