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MEASUREMENT AND CORRELATION OF CONDITIONS FOR ENTRAPMENT AND MOBILIZATION OF RESIDUAL OIL

First Annual Report

Work Performed for the Department of Energy
Under Contract No. DE-AS19-80BC10310

Date Published—September 1982

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New Mexico Petroleum Recovery Research Center
New Mexico Institute of Mining and Technology
Socorro, New Mexico

U. S. DEPARTMENT OF ENERGY

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FOR ENTRAPMENT AND MOBILIZATION OF RESIDUAL OIL**
First Annual Report

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Abstract

This report covers the first year's progress of a project having four major task areas. Substantial progress has been made in each task area, and it is expected that all tasks will be completed during the second (final) year of this project. Work that has been presented during the course of this project and is available in detail in manuscript form (as referenced) is only described briefly in this report.

The first task is to establish the limits of reliability of laboratory waterflooding as an evaluation tool. Wettability is identified as a key variable, and work in the first year has been concentrated on determining the likely wettability conditions given by commonly used laboratory systems. This work is currently being extended to the wetting properties of crude oils and selected aspects of core flooding procedure, such as the effects of overburden pressure and the properties of displaced and displacing fluids.

The second task concerns the effects of high capillary number flows on trapping phenomena and residual oil saturation. Correlations of capillary number and relative permeability behavior at reduced residual saturations have been developed for displacement in sandstones. One application of the correlations is to provide corrections for flushing of residual oil in the region of the wellbore where pressure gradients are abnormally high. Preliminary results have been obtained for two carbonate core samples.

The third task deals with mechanisms of mobilization and entrapment. Detailed accounts have recently been presented of work on relative permeability at reduced residual oil saturations and for factors which affect the magnitude and distribution of residual oil. An extensive study of entrapment and mobilization in bead packs is now largely completed. Close correlation of capillary number relationships for mobilization of oil in bead packs has been achieved for displacements in which interfacial tension and bead size for a given packing were varied. It was found, for bead packs, that capillary numbers for mobilization were more than 20 times higher than those necessary for prevention of entrapment. This difference is greatly reduced by effects of consolidation.

Work on the fourth task concerns the detailed structure of residual oil. The technique of using a nonwetting phase which will solidify and can be separated from the rock has been applied. The size distribution of residual oil blobs, obtained under various displacement conditions, is being measured by various size-analysis methods. A major objective of this work is to determine how blob-size distribution changes as oil recovery progresses, which will, in turn, provide insight into the mechanisms by which residual oil can be recovered.

Task 1. Residual Saturation Measured by Laboratory Core Flooding

Background

The need for accurate determination of residual oil saturation in the swept zone of a waterflood in reservoir evaluation for tertiary oil recovery is now widely recognized. Estimates of the amount of residual oil remaining after waterflooding are often derived from results of laboratory waterflood tests. Incentive for the development of tertiary methods was, for the most part, based on these estimates. When surfactant processes were first field tested, recoveries fell considerably below expectation; low waterflood residuals in the formation were one suspected cause.

The main reasons why laboratory waterflood residuals were generally accepted prior to the advent of tertiary recovery methods, were: (1) apart from estimates of recoverable reserves related to proration allowances, the amount of oil remaining after waterflood was of little economic significance compared to that produced; and (2) it was generally believed that most reservoirs were strongly water-wet and that their condition could be readily simulated in the laboratory in displacements that involved use of suitable brine and a light mineral oil.

Attempts to duplicate displacement in the reservoir are now commonly made by carrying out reservoir-condition laboratory waterfloods. However, there is essentially no standard against which results, even though they may appear reasonable, can be checked. Examples of extreme differences in laboratory waterflood and field measurements of residual oil, which could not be wholly ascribed to problems in sampling, caused loss of acceptance of laboratory measurements as a means of estimating residual oil. For many practical reasons, laboratory-established, residual oil saturations must continue to be used in testing tertiary oil processes, even though these saturations may not be representative of the target formation with respect to either magnitude or distribution. In this respect, test results obtained using Berea outcrop sandstone could be misleading because residual oil saturations in this type of rock appear to be unusually high.

The uncertainties that exist in relating laboratory testing results to the reservoir point to the need for investigation of factors which affect the magnitude and microscopic distribution of residual oil in laboratory flooding tests. The broad objective of this work is to determine the variation of residual oil that can occur in a given core. This will help to identify the problems that can arise in core testing and indicate limits of reliability of laboratory flooding as an evaluation tool for secondary and tertiary recovery.

Wettability variation has been identified as the dominant but least understood variable in core flooding behavior, including retention of residual oil. In the first stage of this work, the likely wettability conditions pertaining to most of the laboratory flooding tests carried out in the present work were investigated through contact angle studies.

Wetting Behavior of Liquids Commonly Used in Displacement Experiments

Laboratory flooding experiments are carried out using various degrees of care in preparation of core samples and test liquids.^{1.1} Small amounts of surface-active material can sometimes have dramatic effects on surface properties which determine wetting behavior, which, in turn, can have a dominant influence on displacement mechanisms. Direct measurements of the wetting properties of laboratory systems are not always feasible. Thus, interpretation of experiments -- for example, comparison of steady- and unsteady-state relative permeabilities -- is often subject to nagging uncertainties as to whether results were unduly influenced by uncontrolled wetting effects. Rates of spontaneous imbibition,^{1.2} in particular, can be very sensitive to relatively minor changes in wetting properties.^{1.3} It is therefore of interest to determine the likely extent of variation of wettability to be expected for commonly used laboratory systems. Results of displacement tests for these systems often serve as a basis for assessing the wetting properties of more complex systems.

Contact angle provides a fundamental measure of wettability. In the present work, we provide a compilation of contact angle results intended to be broadly representative of systems commonly used in laboratory flooding tests. Variables investigated are the oleic and aqueous phases, and the solid substrate.

Experimental

Liquids

Water used in making up aqueous phases was prepared with varying degrees of care:

- 1) Deionized and once distilled using a Corning megapure still.
- 2) Water, distilled as described above, and double-distilled from potassium permanganate solution.
- 3) Tap water (as an example of using water as received).

Brines were made up from analytic grade reagents.

As examples of commonly used laboratory oils, a pure hydrocarbon (analytic grade isooctane) and a fractional distillate (Soltrol 130) were selected. For many of the observations, no special attempts were made to purify further these oils, a main purpose being to determine their wetting behavior when properties of the aqueous phase were varied. For work with purified oil, technical grade isooctane was freed of surface-active impurities by alternating treatments with 1 M sodium hydroxide and fuming sulfuric acid, followed by several washes with double-distilled water.^{1.4}

A variety of solid surfaces were used as substrates. These included fused silica, generally referred to as smooth glass, and roughened sodium silicate glass surfaces, prepared by etching with hydrofluoric acid or by blasting a glass plate with glass shot. Contact angle measurements were also made on surfaces of sandstone and carbonate rocks cut with a diamond saw, and on talc, selected as a clay mineral which could be prepared in the form of a flat surface.

To cause radical change in wetting properties, a few tests were made on glass surfaces treated with diphenyl dichlorosilane. The glass was contacted with solution for about 2 hours (results showed larger contact times to be immaterial), and then baked at 250°C for 1 hour.

Measurement of Contact Angles

A contact angle goniometer, obtained from Gaertner Scientific Corp. of Chicago, was used to measure contact angles. The assembly comprised a protractor and a telescopic objective, coupled to a coordinate positioning stage, which permitted accurate determination of contact angles. A drop of the upper oil phase was formed at a hand-ground, optically flat tip of a thick-walled glass capillary. A micrometer syringe connected to the other end of the capillary enabled the drop size to be varied smoothly. The syringe was suspended from a platform of such rigidity that there was no detectable vibration at the tip when the drop was advanced or receded.

Results and Discussion

Effect of Aqueous Phase and Purification of Oil

Selected results from an extensive series of measurements of advancing and receding angles for Soltrol against various aqueous solutions are listed in Table 1.1. For systems typified by the four sets of results listed in Table 1.1, strongly water-wet conditions and very small contact angle hysteresis were usually observed. Essentially stable contact angles were obtained almost instantaneously. Most angles were observed to be unchanged for at least 10 minutes and in some cases for up to a week. Because of concerns about possible effects of contamination during the course of normal laboratory procedures (such as handling of core specimens) in one series of experiments, the contents of the contact angle cell were deliberately contaminated by immersion of fingers in the water phase by laboratory personnel. No detectable changes in contact angles were observed for the system, which in this particular case gave $\theta_R < \theta_A < 20^\circ$.

The behavior of low, but finite, contact angles observed for a variety of systems was much the same as that experienced by Brown and Neustadter.^{1.5} For a given test, results were usually reproducible within a few degrees, showed only small hysteresis, and were consistent over the whole surface. However, variations of 5-10° were commonly observed for

averaged results of replicate tests, where, for example, the cell is cleaned and fresh solutions are prepared.

Systems were found to remain water-wet even at extremes of pH, although receding and advancing contact angles were about 20° higher (Table 1.3) than both those observed in the present work for moderate variation in pH, and those reported previously by Brown and Neustadter^{1.5} for variation in pH from 3 to 10.

The effect of purification of oil was studied using isooctane. Analytic grade isooctane against once-distilled water gave generally higher advancing contact angles than those observed (Table 1.2) even for tap water. This may have been caused by organic contaminants picked up from a deionizing column used in pretreatment of the once-distilled water. No further attempt was made to determine the cause with more certainty.

In spite of careful efforts to purify liquids and use clean glassware, complete spreading was never observed in the present work. Although spreading has been reported for oil-water systems,^{1.4,1.5} it seems far more difficult to achieve high-energy surfaces than might be expected. Very little appears to be known about the cause of variation in advancing contact angles in the range of about 15 - 35° . However, provided contact angles remain within this range, the consequent effect of equivalent variation in wetting behavior of porous media is not likely to be of great significance with respect to displacement behavior.^{1.6}

Addition of a Trivalent Cation

Recent investigations of aqueous solutions against air have shown that contact angle^{1.7} can change with charge on the solid surface. Some evidence for this type of behavior was found for oil-water systems containing small amounts of aluminum in the aqueous phase. Advancing angles were observed to increase (Table 1.4) and showed sensitivity to pH. Throughout the range of contact angle change, the solid remained preferentially wetted by the aqueous phase.

Because of interest in the possibility of obtaining some degree of wettability control at high-energy surfaces through variation in ionic species and concentration, either for laboratory use or practical applications, further measurements were made on aqueous phases containing aluminum ions. With roughened glass surfaces (prepared either by sand blasting or etching with hydrofluoric acid) or sandstone as substrate, contact angles remained low. If the advancing contact angles had been about 43 - 56° , as observed at smooth surfaces, previous observations of the effect of roughness on contact angle^{1.8} indicate that even higher contact angles would be observed for the roughened glass. With air as the nonwetting phase instead of oil, contact angles for solution containing Al^{+++} ions were low ($\theta_R \sim 15^\circ$, $\theta_A \sim 18^\circ$). Furthermore, for Al^{+++} solution, rates of spontaneous imbibition and capillary imbibition displacement pressures for glass beads did not show shifts from results for low contact angle systems that might be expected^{1.3,1.6,1.9} if advancing contact

angles corresponded to smooth surface values of about 50° . Thus, the advancing contact angle behavior observed for Al^{+++} solution against Soltrol at smooth surfaces must for the present remain a curiosity that could not be confirmed by other measurements.

Oil-Alcohol-Brine

Oil-alcohol-brine systems have been used as a convenient method of obtaining two-phase systems for which interfacial tension can be adjusted reliably through alcohol content.^{1.10} In this role, alcohols are regarded as model amphiphiles in investigation of surfactant behavior.^{1.10-1.12} There is evidence that alcohols adsorb at silica interfaces.^{1.13,1.14} In tests for possible changes in wetting properties that might be caused by such adsorption, measurements were made on the systems listed in Table 1.5. For all compositions tested, strong aqueous-phase wetting was observed at both smooth and roughened silica surfaces; however, in no case was spreading observed. Contact angle hysteresis was generally low but somewhat higher for roughened surfaces.

Silane-Treated Glass

Treatment of glass with dimethyl-dichlorosilane lead to strongly oil-wet conditions. Advancing and receding contact angles through the aqueous phase for oil-water and oil-alcohol-water systems at both rough and smooth substrates all fell within the range of $150-170^\circ$. The low, but finite contact angles and low contact angle hysteresis exhibited by the oil phase for the particular silane treatment employed were thus broadly comparable to the angles observed through the water phase for untreated glass. In such cases, it appears highly reasonable to describe wettability as having been reversed. Lower contact angles could be obtained by more moderate treatments.

Sandstone, Carbonate and Clay Surfaces

Advancing and receding contact angles were measured on Berea and Tensleep sandstones, carbonate, and talc surfaces. In all cases where low receding and advancing angles had been observed for smooth or roughened silica, similar low contact angles were also observed for the porous rocks.

Conclusions

1. Strongly water-wet conditions ($\theta_R < \theta_A < 30^\circ$), but not complete wetting ($\theta_R = \theta_A = 0^\circ$), will usually be obtained in sand and bead packs and in clean sandstones such as Berea, using refined mineral oils or other hydrocarbons as the oil phase, and water or some form of brine as the wetting phase.

2. Brine/isopropyl alcohol/isooctane systems at silica substrates were strongly wetting with respect to the aqueous phase over a wide range of interfacial tensions given by variation in composition.

3. Strong wetting by the oleic phase ($\theta_A > \theta_R > 150^\circ$ through water phase) for both oil-water and oil-alcohol-water can be obtained for silane-treated silica substrates.

4. Systems exhibiting low contact angles at either smooth or rough silica surfaces also gave low contact angles on talc and at clean sandstone and carbonate rock surfaces.

References

- 1.1 Culec, L., "Study of Problems Related to the Restoration of the Natural State of Core Samples," J. Can. Pet. Tech. 16, No. 4 (Oct.-Dec. 1977) 68-80.
- 1.2 Bobek, J. E. and Mattax, C. C., "Reservoir Rock Wettability-Its Significance and Evaluation," Trans. AIME; J. Pet. Tech. (July 1958).
- 1.3 McCaffery, F. G. and Bennion, D. W., "Experimental Study of the Relationship of Contact Angles to Imbibition in Porous Media," Preprints, 48th National Colloid Symposium, Div. of Coll. and Surface Chem., Amer. Chem. Soc., June 24-26, 1974, 124-129.
- 1.4 McCaffery, F. G. and Mungan, N., "Contact-Angle and Interfacial Tension Studies of Some Hydrocarbon-Water-Solid Systems," J. Can. Pet. Tech. (July-Sept. 1970) 185.
- 1.5 Brown, C. E. and Neustadter, E. L., "The Wettability of Oil/Water/Silica Systems with Reference to Oil Recovery," J. Can. Pet. Tech. (July-Sept. 1980) 100-110.
- 1.6 Morrow, N. R. and McCaffery, F. G., "Displacement Studies in Uniformly Wetted Porous Media," in Wetting, Spreading and Adhesion, Ed. J. F. Padday, Academic Press, New York (1978) 289-319.
- 1.7 Ottewill, R. H., Billett, D. F., Gonzalez, G., Hough, D. B., and Lovell, V. M., "The Variation of Contact Angle at the Silver Iodide-Liquid-Vapor Interface with the Charge on the Solid Surface," in Wetting, Spreading and Adhesion, Ed. J. F. Padday, Academic Press, New York (1978) 183-199.
- 1.8 Morrow, N. R., "The Effects of Surface Roughness on Contact Angle with Special Reference to Petroleum Recovery," J. Can. Pet. Tech. (Oct.-Dec. 1975).
- 1.9 Melrose, J. C., "Wettability as Related to Capillary Action in

Porous Media," Soc. Pet. Eng. J. (Sept. 1965) 259.

- 1.10 Knickerbocker, B. M., Pesheck, C. V., Scriven, L. E., and Davis, H. T., "Phase Behavior of Alcohol-Hydrocarbon-Brine Mixtures," J. Phys. Chem. 83, No. 15 (1979) 1984-1990.
- 1.11 Puig, J. E., Hemeker, D., Gupta, A., Scriven, L. E., and Davis, H. T., "Interfacial Tensions of Alcohol-Hydrocarbon-Brine Systems," J. Phys. Chem., to be published (1981).
- 1.12 Teletzke, G. F., Scriven, L. E., and Davis, H. T., "Patterns of Wetting Behavior in Multicomponent Systems," SPE 10112, presented at the 56th Annual Fall Technical Conference and Exhibition of SPE of AIME, San Antonio, TX, Oct. 5-7, 1981.
- 1.13 Knozinger, H. and Stahlin, W., "Adsorption of Alcohols on Silica-Evidence for the Existence of Aprotic Adsorption Sites," Progress in Coll. and Polym. Sci. 67 (1980) 33-40.
- 1.14 Oscik, J., Goworek, J., and Kusak, R., "Adsorption of Aliphatic Alcohols from Benzene Solutions on Silica Gel," J. Coll. Inter. Sci. 79, No. 2 (1981) 308-312.

Table 1.1 Receding and Advancing Contact Angles for
Oil/Aqueous Solution Systems on Smooth Silica

Nonwetting Phase (Drop)	Aqueous Phase	pH of Aqueous Phase	θ_R	θ_A
Soltrol 130	Water (dd)	5.80	21.2° ($\pm 3.3^\circ$)	19.9° ($\pm 2.1^\circ$)
Soltrol 130	2% CaCl_2	6.19	14.9° ($\pm 1.9^\circ$)	16.1° ($\pm 1.9^\circ$)
Soltrol 130	1% $\text{Na}_5\text{P}_3\text{O}_{10}$	9.45	16.0° ($\pm 2.2^\circ$)	17.1° ($\pm 2.4^\circ$)
Soltrol 130	6% NaCl	6.35	15.4° ($\pm 1.4^\circ$)	16.1° ($\pm 1.8^\circ$)

Table 1.2 Receding and Advancing Contact Angles on Smooth
Silica for Unpurified and Purified Isooctane

Phases		θ_R	θ_A
Oleic	Aqueous		
unpurified isooctane	twice-distilled water from KMnO_4	14.1° ($\pm 0.9^\circ$)	19.6° ($\pm 1.0^\circ$)
"	once-distilled water	22.2° ($\pm 1.3^\circ$)	36.0° ($\pm 1.0^\circ$)
"	local tap water	14.2° ($\pm 1.2^\circ$)	23.5° ($\pm 2.8^\circ$)
purified isooctane	twice-distilled water from KMnO_4	11.3° ($\pm 1.5^\circ$)	17.3° ($\pm 1.3^\circ$)
"	once-distilled water	12.8° ($\pm 1.5^\circ$)	17.0° ($\pm 1.1^\circ$)

Table 1.3 Effect of Extremes of pH on Advancing and Receding Contact Angles on Smooth Silica

Oil Drop	pH	Acid or Alkali Used	θ_R	θ_A
(1) isooctane	12.50	NaOH	37.0° ($\pm 3.5^\circ$)	47.0° ($\pm 3.4^\circ$)
(2) isooctane	5.80	(water)	20.7° ($\pm 2.5^\circ$)	21.9° ($\pm 1.7^\circ$)
(3) isooctane	1.00	HCl	33.3° ($\pm 1.8^\circ$)	39.3° ($\pm 6.0^\circ$)

Table 1.4 Receding and Advancing Contact Angles for
Solutions Containing Aluminum Ions

(a) Smooth Silica as Substrate

Nonwetting Phase (Drop)	Aqueous Phase	pH of Aqueous Phase	θ_R	θ_A
Soltrol 130	0.06% $Al_2(SO_4)_3$	4.0	19.3° ($\pm 1.8^\circ$)	28.2° ($\pm 2.7^\circ$)
Soltrol 130 } 	0.006% $Al_2(SO_4)_3$ in 1.5% $CaCl_2^*$	4.0	18.1° ($\pm 2.4^\circ$)	43.1° ($\pm 4.2^\circ$)
		4.7	20.0° ($\pm 3.1^\circ$)	53.2° ($\pm 5.6^\circ$)
		7.6	20.6° ($\pm 2.3^\circ$)	45.6° ($\pm 4.0^\circ$)

(b) Sandstone as Substrate

Phases			θ_R	θ_A
Oleic	Aqueous	Solid		
purified isooctane	solution α	Berea sandstone	20.0° ($\pm 1.1^\circ$)	30.6° ($\pm 1.7^\circ$)
purified isooctane	solution α	Tensleep sandstone	23.8° ($\pm 1.1^\circ$)	33.9° ($\pm 1.4^\circ$)

* Referred to as solution α for pH 4.7

Table 1.5 Advancing and Receding Contact Angles for Oil/Alcohol/Water Systems at Smooth and Roughened Glass Surfaces

Percentage of Components in Two-Phase System			SUBSTRATE Aqueous Phase	SMOOTH SILICA 2% CaCl ₂		SMOOTH SILICA Double-Distilled Water		ROUGHENED SILICA Double-Distilled Water	
Aqueous Phase	IPA	Iso-octane	Interfacial Tension (dynes·cm ⁻¹)	θ_R	θ_A	θ_R	θ_A	θ_R	θ_A
75	5	20	21.5 (± 0.96)	15.6° ($\pm 2.0^\circ$)	20.3° ($\pm 1.4^\circ$)				
71	9	20	18.4 (± 0.51)	16.6° ($\pm 2.9^\circ$)	27.5° ($\pm 5.6^\circ$)	17.1° ($\pm 4.8^\circ$)	21.0° ($\pm 1.0^\circ$)	21.2° ($\pm 1.1^\circ$)	31.0° ($\pm 1.0^\circ$)
70	12	18	15.7 (± 0.52)	15.9° ($\pm 1.3^\circ$)	19.3° ($\pm 1.5^\circ$)				
64	15	21	11.6 (± 0.17)	21.5° ($\pm 1.5^\circ$)	21.6° ($\pm 2.0^\circ$)	16.1° ($\pm 0.4^\circ$)	21.3° ($\pm 1.1^\circ$)	21.8° ($\pm 2.1^\circ$)	30.4° ($\pm 0.3^\circ$)
58	20	22	6.2 (± 0.19)	21.1° ($\pm 1.5^\circ$)	25.7° ($\pm 1.9^\circ$)				
54	27	19	4.37 (± 0.31)	19.0° ($\pm 2.6^\circ$)	22.4° ($\pm 2.1^\circ$)	15.7° ($\pm 0.7^\circ$)	21.3° ($\pm 0.03^\circ$)	16.1° ($\pm 1.7^\circ$)	20.6° ($\pm 2.1^\circ$)
43	38	19	2.10 (± 0.23)	16.5° ($\pm 3.2^\circ$)	20.6° ($\pm 1.5^\circ$)				
34	48	18	1.15 (± 0.23)	13.7° ($\pm 5.1^\circ$)	14.9° ($\pm 6.1^\circ$)	13.1° ($\pm 1.0^\circ$)	17.3° ($\pm 1.0^\circ$)		

Task 2. Effect of High Pressure Gradients and Residual Oil Saturations

Background

For tertiary recovery prospects under serious consideration, residual oil saturations are now being determined by in situ methods. These include pressure coring, new and improved logging techniques, and tracer tests. No single method of measurement is widely accepted, and each has its own particular advantages and disadvantages. The need for accurate measurements of residual oil is so acute that it is now recommended that a suite of measurements be taken, all of which are expensive, to obtain a best estimate of residual oil saturation.

Except for the tracer method, the more favored methods of measuring residual oil involve pressure cores and/or specialized logging techniques that involve the relatively small portion of the reservoir close to the wellbore. Both the pressure cores and the wellbore region will have been subjected to abnormally high pressure gradients as compared with the rest of the formation. The pressure gradients may be high enough to cause significant flushing of the oil from the cores or from the region close to the wellbore as compared with the formation as a whole.

Corrections for the effects of high flow rate to in situ measurements of residual oil require knowledge of capillary number relationships (relationships between the ratio of viscous to capillary forces and reduction in residual oil saturation) and relative permeabilities at reduced residual saturation. Capillary number relationships and their application to corrections for residual oil flushing are now being extended to include work on carbonate rocks and the effects of rock wettability. General correlations for residual oil flushing will be sought.

a) Correlated Capillary Number Relationships for Sandstones

Results of capillary number relationships obtained for a wide range of sandstone during the course of studying residual oil behavior have been presented. A best fit to the data obtained is shown in Fig. 2.1. This correlation is now being used in calculations of flushing in the wellbore region.

Capillary number relationships have also been obtained for a carbonate rock sample. Results fell very close to the curve shown in Fig. 2.1 for sandstones.

b) Relative Permeabilities at Reduced Residual Saturations

In addition to correlations of capillary number relationships, attention has been given to relative permeabilities at reduced residual

2.1 saturations. Results for displacement of discontinuous oil typical of a large body of data, free of what were judged to be obvious abnormalities, are presented in Fig. 2.2. The data are seen to fall within a reasonably narrow band. Rather than taking a best statistical fit of all assembled data, the fitted S-shaped curve (hereafter referred to as the S curve) was drawn somewhat subjectively with bias towards those results which, not only appeared more valid, but also behaved self-consistently, for example, with respect to volumetric and gravimetric material balances during the course of measurement.

In addition to data points for relative permeabilities at reduced residual saturations falling close to the S curve shown in Fig. 2.2, a relationship was also observed between normal waterflood residual saturation, S_{or}^* , and relative permeability to water, k_{rw}^* , usually measured at flow rates close to critical. The k_{rw}^* vs. S_{or}^* relationship, in effect, provided an extension of the lower portion of the S curve and reaffirmed the strong dependence of k_{rw} on the magnitude of the corresponding residual oil saturation for water-wet systems.

We denote the relative permeability at reduced residual oil saturation arrived at by displacement of discontinuous oil as $k_{rw,d}$. The S curve for $k_{rw,d}$ vs. S_{or} ($S_{or} = 1 - S_w$; $S_w > 1 - S_{or}^*$) is not completely general but may be reasonably representative of flow behavior under water-wet conditions for a fairly wide range of lithologic types of consolidated sandstones. With regard to the general problem of correlation of $k_{rw,d}$ vs. S_{or} relationships, the S curve can be used in the absence of other information. If k_{rw}^* and S_{or}^* are known and they do not fall on the S curve, it is suggested that the curve be adjusted by linear scaling. A new $k_{rw}-S_{or}$ curve, beginning at the given point (k_{rw}^* , S_{or}^*) is generated by scaling $S_{or,s}$ by the factor $S_{or}^*/S_{or,s}$, where S_{or}^* is the saturation of the given sample at the observed permeability k_{rw}^* , and $S_{or,s}$ is the saturation corresponding to k_{rw}^* but given by the S curve. $S_{or,s}$ is the saturation value taken from the S curve at the selected value of $k_{rw,d}$. Other observations relating relative permeabilities to displacement mechanisms are summarized under Task 3b.

c) Correction to In Situ Measurements of Residual Oil for Flushing at the Wellbore

Work is now proceeding on applying the correlated capillary number and relative permeability relationships to providing corrections for the effects of flushing around the wellbore. Main variables considered are the formation permeability and the overbalance pressure.

Reference

- 2.1 Morrow, N. R., Chatzis, I., and Lim, H. T., "Relative Permeabilities at Reduced Residual Saturations," presented at International Energy Agency Workshop, Winfrith, U.K., Sept. 1981.

FIGURE 2.1. RESULTS FOR MOBILIZATION OF OIL FROM A CARBONATE ROCK AND CAPILLARY NUMBER CORRELATION DEVELOPED FROM RESULTS FOR A LARGE NUMBER OF SANDSTONES.

FIGURE 2.2. DATA USED TO OBTAIN S CURVE RELATIONSHIP BETWEEN RELATIVE PERMEABILITY TO WATER AND REDUCED RESIDUAL OIL SATURATION.

Task 3. Mechanisms of Mobilization and Entrapment of Residual Oil

Background

Task 3 involves study of oil trapping and recovery mechanisms at the microscopic level. Work on this task is divided into three main areas as indicated below.

a) Magnitude and Detailed Structure of Residual Oil Saturation^{3.1}

A full report on this work was presented at the SPE/DOE Symposium on Improved Oil Recovery. Copies of the preprint^{3.1} SPE/DOE 10681 are available from the authors upon request. Discussion of some aspects of this work relating to blob-size distribution is given under Task 4.

b) Relative Permeabilities at Reduced Residual Saturations^{3.2}

A detailed account of this work has been presented^{3.2} and manuscripts are available upon request. Conclusions from this work were as follows:

1. For water-wet conditions in sandstones having a wide range of permeabilities, relative permeabilities to water, k_{rw} , at reduced residual saturations, S_{or} , achieved by high capillary number displacements were highly sensitive to remaining oil saturation.

2. Relative permeabilities, $k_{rw,d}$, measured after displacement of discontinuous oil, were correlated satisfactorily (for the tested sandstone) by an S-shaped curve.

3. Comparison of values of $k_{rw,d}$ (given by displacement of initially discontinuous oil) of the present work with previously reported measurements of relative permeability for initially continuous oil, $k_{rw,c}$, suggests that $k_{rw,c}$ is significantly less than $k_{rw,d}$ at a given value of reduced residual oil saturation. Limited data obtained in the present work showed much less difference.

4. Relative permeabilities, k_{rw}^* , at waterflood residuals, S_{or}^* , for the various tested sandstones, showed strong dependence on the magnitude of S_{or}^* . Relationships between S_{or}^* and k_{rw}^* directly merged with and extended the high oil saturation portions of the correlation between $k_{rw,d}$ and S_{or} .

5. Relative permeabilities $k_{rw,c}$ at reduced residual saturations in unconsolidated media are generally lower than values of $k_{rw,d}$ for well cemented sandstones.

6. Relative permeabilities at normal waterflood residual saturation,

S_{or}^* , were often sensitive to pressure gradient and usually decreased with increase in pressure gradient. At a given reduced oil saturation, S_{ro} , k_{rw} was independent of pressure gradient.

7. Relative permeabilities, $k_{rw,d}$, were correlated for almost an order of magnitude reduction of normal oil-water interfacial tensions.

8. A variety of indirect evidence suggests that water channeling is a dominant feature of the increase in water permeability that accompanies mobilization of residual oil.

c) Capillary Number Measurements for Displacement of Residual Oil from Unconsolidated Bead Packs

Special attention has been given to the mechanisms of mobilization and prevention of entrapment in bead packs. These idealized media were investigated for the following reasons:

- (1) Standard results provided can be checked by other investigators.
- (2) Permeability can be varied while the media remains geometrically scaled in a statistical sense.
- (3) Close-sized bead and sand packs are the most commonly used form of porous media.
- (4) Unconsolidated media provide a distinct class of pore geometry.
- (5) A basis is provided for interpreting tests on oil recovery processes carried out in unconsolidated media.

The following topics are being investigated:

- (1) Capillary numbers for mobilization of trapped oil including a direct test of the capillary number concept with variation in interfacial tension and bead size (permeability).
- (2) Comparison of capillary number versus residual oil saturation relationships for displacement of continuous oil and discontinuous oil.
- (3) Comparison of capillary number relationships, for unconsolidated beads, partially sintered beads, and well consolidated sandstones.
- (4) Relative permeabilities at reduced residual oil satu-

rations.

- (5) Comparison of trapping of air and oil as nonwetting phases.

EXPERIMENTAL

Fluids:

Equilibrated liquid pairs were obtained by mixing predetermined quantities of IPA, isooctane and 2% brine to give systems of desired interfacial tension. The upper phase was rich in isooctane and from contact angle measurements (see results under Task 1) was confirmed to be the nonwetting phase. Phase behavior, interfacial tensions, densities and viscosities of these systems have been presented previously.^{3,4}

Apparatus:

The beads were packed in a glass chromatographic column, having internally threaded glass ends (Fig. 3.1). The column had an internal diameter of 2.5 cm and length of 30 cm. The tube was fitted with threaded Teflon end pieces. A glass frit of pore size 10-20 microns was sealed into the lower end using epoxy resin. A circular PTFE screen and polyethylene washer were inserted at the upper end.

Preparation of Column:

All solutions were de-aired by placing under vacuum and suspending in an ultrasonic bath prior to use. The bottom fitting was put in place with an O-ring and flooded at high pressure to ensure removal of all air from the frit. The upper portion of the glass tube was wiped dry; then the column was weighed with the lower phase being in and below the frit. More of the lower phase was added, and beads were added next, slowly and carefully, to avoid trapping of air. Formation of uniform packings was aided by vibration during the packing procedure. With the column filled with sufficient beads (of known weight) to ensure a fixed packing, the Teflon end cap was filled with lower phase and weighed together with the screen and O-ring, and attached to the column. The seal in the upper part of the column was checked by flooding the column with lower phase at high injection pressure. The column was then disconnected and weighed.

Establishing Irreducible Wetting Phase Saturation:

Lower phase in the column was displaced with upper phase by gravity. The column was set to provide drainage of all of the given bead pack to the irreducible saturation but was kept well below the penetration pressure of the glass frit. Space below the frit remained completely

filled with lower phase at all times. The column was allowed to drain for about 24 hrs. Initial water saturation was determined from the column weight.

Displacement of Residual Oil:

The column was flooded with lower phase at low capillary number to give a normal residual saturation of the nonwetting phase. The column was then flooded at increasing flow rates (i.e., at higher capillary numbers). Two pore volumes were passed through the column at each selected flooding rate. After flooding at a given rate, the column was weighed to obtain the residual saturation. All runs were carried out by using a constant pressure pump.

Bead size was selected in such a way that an inverse Bond number was always kept above 200, thus eliminating any effect of buoyancy on residual oil saturation.^{3.3}

Results and Discussion

Mobilization of Trapped Oil

Results obtained for four sizes of beads at interfacial tensions ranging from 17.0 down to 2.8 dynes/cm for mobilization of discontinuous oil are listed in Table 3.1(a, b, c, d), and plots of residual saturation versus capillary number are presented in Figs. 3.2-3.5. Excellent reproducibility was obtained for a given system, and the capillary number gave close correlation for variation in permeability, interfacial tension, and viscosity (Fig. 3.6). These results are probably the most definitive experimental support yet provided for the capillary number correlation.

Results for prevention of entrapment were obtained previously for trapping of gas as the nonwetting phase.^{3.3,3.4} It was known that results for mobilization of trapped gas gave a lower limit of the capillary number curve because of observed solution effects. Results obtained for mobilization of residual oil, presented in Figs. 3.2 through 3.5, showed capillary numbers for mobilization in bead packs to be much higher than expected, being even higher than the values for cores of narrow and wide pore-size distribution reported by Foster.^{3.5} Capillary numbers for mobilization of residual oil in unconsolidated media are 25 times higher than values required for prevention of entrapment (Fig. 3.7). This difference is much greater than differences observed for sandstones (Fig. 3.8), and extends over a much greater range of relative reduction in residual oil.

Preliminary results for sintered beads (Fig. 3.8) show that consolidation of beads greatly reduces the differences between capillary number for mobilization and entrapment. It is believed that increase in aspect ratio (pore-body to pore-throat size) is the main cause of the

observed reduction. Note that for the results shown in Fig. 3.7, the differences between the mobilization and entrapment decreases as permeability decreases. Decrease in aspect ratio is always a likely cause of reduction in permeability, because permeability is largely controlled by pore throat size. Investigation of the effect of relative pore throat size on oil recovery is being continued.

References

- 3.1 Chatzis, I., Morrow, N. R., and Lim, H. T., "Magnitude and Detailed Structure of Residual Oil Saturation," SPE 10681, presented at 1982 SPE/DOE Third Joint Symposium on Enhanced Oil Recovery, Tulsa, OK, April 4-7, 1982.
- 3.2 Morrow, N. R., Chatzis, I., and Lim, H. T., "Relative Permeabilities at Reduced Residual Saturations," presented at International Energy Agency Workshop, Winfrith, Sept. 1981.
- 3.3 Morrow, N. R. and Songkran, B., "Effect of Viscous and Buoyancy Forces on Nonwetting Phase Trapping in Porous Media," in Surface Phenomena in Enhanced Oil Recovery, Ed. D. O. Shah, Plenum Press, New York, 1981.
- 3.4 Morrow, N. R. and Chatzis, I., "Measurement and Correlation of Conditions for Entrapment and Mobilization of Residual Oil," Final Report to the U.S. Department of Energy, Report No. DOE/BETC/3251-12, Oct. 1981.
- 3.5 Foster, W. R., "A Low-Tension Waterflooding Process," J. Pet. Tech. 25 (Feb. 1973) 205.

Table 3.1(a) Capillary Number versus Residual Oil for Bead Packs

Bead Size 45-50 mesh $\sigma = 17.0$ dynes/cm Bond Number 0.00475

Flow Rate cc/min	Capillary No. $v\mu/\sigma$	Reduced Residual Oil %	Normalized Reduced Residual
2.33	6.2×10^{-6}	16.24	1.0
260.9	6.97×10^{-4}	14.59	0.90
380.95	1.02×10^{-3}	13.96	0.86
444.44	1.19×10^{-3}	13.77	0.85
558.14	1.49×10^{-3}	13.62	0.84
681.82	1.82×10^{-3}	13.48	0.83
750.0	2.0×10^{-3}	12.65	0.78
857.14	2.29×10^{-3}	11.88	0.73
983.61	2.63×10^{-3}	10.67	0.66
1153.8	3.08×10^{-3}	8.05	0.50
1363.64	3.65×10^{-3}	6.45	0.40
1578.95	4.22×10^{-3}	4.8	0.30

Table 3.1(b) Capillary Number versus Residual Oil for Bead Packs

Bead Size 60-70 mesh $\sigma = 11.8$ dynes/cm Bond Number 0.00329

Run No.	Flow Rate cc/min	Capillary No. $v\mu/\sigma$	% Reduced Residual Oil	Normalized Reduced Residual
1	3.33	1.7×10^{-5}	16.01	1.0
	75	3.8×10^{-4}	15.63	0.98
	250	1.28×10^{-3}	15.38	0.96
	338	1.73×10^{-3}	15.15	0.95
	500	2.55×10^{-3}	11.84	0.74
	600	3.1×10^{-3}	10.04	0.63
	697.7	3.6×10^{-3}	8.47	0.53
	769.2	3.9×10^{-3}	7.46	0.47
	833.33	4.25×10^{-3}	6.12	0.38
	882	4.5×10^{-3}	4.86	0.30
	937.5	4.8×10^{-3}	4.27	0.27
	1071.4	5.5×10^{-3}	3.31	0.21
	1250	6.38×10^{-3}	2.86	0.18
	1500	7.7×10^{-3}	2.76	0.17
2	3.33	1.7×10^{-5}	14.43	1.0
	23.72	1.2×10^{-4}	14.21	0.98
	150	7.66×10^{-4}	13.72	0.95
	188.98	9.65×10^{-4}	13.54	0.94
	269.66	1.38×10^{-3}	13.42	0.93
	416.67	2.13×10^{-3}	12.04	0.83
	779.22	3.98×10^{-3}	4.26	0.30
	1111.11	5.67×10^{-3}	0.82	0.06
	1428.6	7.29×10^{-3}	0.46	0.03
3 (Column repacked)	3.33	2.07×10^{-5}	15.81	1.0
	172.66	8.8×10^{-4}	14.66	0.93
	319.15	1.63×10^{-3}	14.51	0.92
	416.7	2.13×10^{-3}	13.23	0.84
	576.92	2.95×10^{-3}	9.96	0.63
	789.5	4.03×10^{-3}	5.98	0.38
	845.1	4.31×10^{-3}	4.9	0.31
	1052.6	5.37×10^{-3}	3.7	0.23
	1304.35	6.66×10^{-3}	2.73	0.17
	1428.6	7.29×10^{-3}	2.43	0.15
	1500	7.66×10^{-3}	2.15	0.14

Table 3.1(c) Capillary Number versus Residual Oil for Bead Packs

Bead Size 70-80 mesh $\sigma = 6.6$ dynes/cm Bond Number 0.00406

Run No.	Flow Rate cc/min	Capillary No. $v\mu/\sigma$	% Reduced Residual Oil	Normalized Reduced Residual
1	1.67	2.07×10^{-5}	14.79	1.0
	26.1	3.25×10^{-4}	14.16	0.96
	61.2	7.6×10^{-4}	13.63	0.92
	127.66	1.59×10^{-3}	13.44	0.91
	155.8	1.93×10^{-3}	13.44	0.91
	188.98	2.35×10^{-3}	12.68	0.86
	218.18	2.7×10^{-3}	11.78	0.8
	250	3.1×10^{-3}	10.83	0.73
	272.7	3.39×10^{-3}	9.98	0.67
	292.68	3.6×10^{-3}	9.19	0.62
	307.7	3.8×10^{-3}	7.76	0.52
	324.32	4.03×10^{-3}	6.87	0.46
	352.9	4.4×10^{-3}	5.4	0.37
	375	4.7×10^{-3}	5.4	0.37
	413.8	5.15×10^{-3}	5.23	0.35
	833	1.02×10^{-2}	0.74	0.05
	882.35	1.1×10^{-2}	0.26	0.02
2	1.67	2.07×10^{-5}	14.27	1.0
	22.7	2.82×10^{-4}	14.06	0.99
	60	7.46×10^{-4}	13.53	0.95
	96.8	1.2×10^{-3}	13.53	0.95
	179	2.23×10^{-3}	12.87	0.90
	283	3.5×10^{-3}	9.78	0.69
	365.9	4.55×10^{-3}	7.37	0.52
	428.57	5.3×10^{-3}	6.08	0.43
	476.2	5.9×10^{-3}	4.55	0.32
	508.5	6.3×10^{-3}	3.86	0.27
	517.24	6.4×10^{-3}	3.41	0.24
	576.9	7.2×10^{-3}	1.82	0.13
	612.2	7.6×10^{-3}	1.24	0.087
	882.35	1.1×10^{-2}	0.16	0.011
3	1.67	2.07×10^{-5}	13.87	1.0
	14.08	1.75×10^{-4}	13.75	0.99
	42.3	5.3×10^{-4}	13.28	0.96
	181.82	2.26×10^{-3}	12.85	0.93
	300	3.73×10^{-3}	9.44	0.68
	468.75	5.83×10^{-3}	5.21	0.38
	500	6.22×10^{-3}	3.99	0.29
	521.74	6.49×10^{-3}	2.96	0.21
	645.16	8.02×10^{-3}	1.69	0.12
	714.29	8.9×10^{-3}	1.43	0.10

Table 3.1(d) Capillary Number versus Residual Oil for Bead Packs

Bead Size 100-120 mesh $\sigma = 2.8$ dynes/cm Bond Number 0.0043

Run No.	Flow Rate cc/min	Capillary No. $v\mu/\sigma$	% Reduced Residual Oil	Normalized Reduced Residual
1	1.33	4.7×10^{-5}	15.02	1.0
	16.13	5.69×10^{-4}	14.04	0.935
	57.69	2.04×10^{-3}	12.6	0.84
	137.9	4.87×10^{-3}	6.7	0.45
	176.47	6.23×10^{-3}	3.14	0.21
	214.29	7.56×10^{-3}	1.05	0.07
	294.12	1.03×10^{-2}	--	--
2	1.33	4.7×10^{-5}	15.17	1.0
	3.33	1.18×10^{-4}	15.17	1.0
	15.63	5.36×10^{-4}	13.86	0.914
	36.59	1.29×10^{-3}	13.23	0.87
	65.93	2.33×10^{-3}	12.66	0.84
	92.31	3.26×10^{-3}	10.39	0.69
	122.45	4.32×10^{-3}	7.57	0.49
	171.43	6.05×10^{-3}	3.65	0.24
	211.27	7.45×10^{-3}	1.95	0.099
	265.49	9.37×10^{-3}	0.81	0.053
	294.12	1.04×10^{-2}	0.75	0.049
	352.94	1.25×10^{-2}	0.50	0.033

(a) LOWER END PLUG

(b) COLUMN

(c) ARRANGEMENT FOR DRAIN-
AGE AND PERMEABILITY
MEASUREMENTS

FIGURE 3.1. APPARATUS FOR MEASUREMENT OF CAPILLARY NUMBER RELATIONSHIPS AND RELATIVE PERMEABILITIES OF REDUCED RESIDUAL SATURATION.

FIGURE 3.2. RESIDUAL OIL SATURATION vs CAPILLARY NUMBER
FOR MOBILIZATION IN 45-50 MESH BEAD PACKS.
(RADIUS, 162 microns ; INTERFACIAL TENSION, 17.0 dynes/cm).

FIGURE 3.3. RESIDUAL OIL SATURATION vs CAPILLARY NUMBER
FOR MOBILIZATION IN 60-70 MESH BEAD PACKS.
(RADIUS, 115 microns; INTERFACIAL TENSION, 11.8 dynes/cm).

FIGURE 3.4. RESIDUAL OIL SATURATION vs CAPILLARY NUMBER
FOR MOBILIZATION IN 70-80 MESH BEAD PACKS.
(RADIUS, 97 microns, INTERFACIAL TENSION, 6.6 dynes/cm)

FIGURE 3.5. RESIDUAL OIL SATURATION vs CAPILLARY NUMBER
FOR MOBILIZATION IN 100-120 MESH BEAD PACKS.
(RADIUS, 70 microns, INTERFACIAL TENSION, 2.8 dynes/cm)

FIGURE 3-6. REDUCED RESIDUAL SATURATION vs CAPILLARY NUMBER FOR ALL RESULTS OBTAINED FOR BEAD PACKS. (See Figure 3-2 - 3-5).

FIGURE 3.7. COMPARISON OF RESULTS FOR MOBILIZATION AND PREVENTION OF ENTRAPMENT IN BEAD PACKS.

FIGURE 3.8. COMPARISON OF CAPILLARY NUMBERS FOR MOBILIZATION OF RESIDUAL OIL IN UNCONSOLIDATED BEAD PACKS, SINTERED BEAD PACKS AND SANDSTONES.

Task 4. Residual Oil Structure

Background

In addition to the amount of residual oil, the microscopic distribution of residual oil within the pore spaces of a reservoir rock is also important to the mechanism of tertiary recovery. For example, in modeling the recovery of residual oil, the viscous force required for mobilization is expected to be inversely proportional to ganglia length.^{4.1-4.3} The technique^{4.4,4.5} of using a nonwetting phase which after flooding to residual saturation, can be solidified and then separated from the porous matrix has been used to study the microscopic structure of residual nonwetting phase. The isolated, irregularly shaped, capillary structures are often described as blobs. Although considerable attention has been paid to the obviously important subject of residual oil structure, the amount of quantitative information on blob structure and the statistics of blob populations is very limited.

One of the recent needs for such information is the testing of theories of displacement which lead to predictions of blob-size distributions. To obtain such information, satisfactory techniques for preparing statistically representative samples must be developed; these samples must be amenable to analysis.

Experimental Work

The techniques used to study the microscopic structure of residual oil in our laboratory and to obtain statistics on how residual oil is distributed at the microscopic scale of pores involved the following:

- 1) Use of the fluid pair styrene monomer-2% CaCl_2 brine. After waterflooding the styrene monomer to residual saturation, the trapped styrene was polymerized in situ by heating. The solidified styrene blobs were separated from the porous matrix by leaching the porous rock with mineral acids. Details of the core flooding procedure, in situ polymerization of the trapped styrene, and recovery of oil blobs are given elsewhere.^{4.6}
- 2) Taking scanning electron micrographs (SEM) of typical oil blobs found in a given core sample after waterflooding to residual oil at various capillary numbers.
- 3) Obtaining statistics of blob-size distribution of residual oil, by particle analyses performed on representative populations of recovered styrene blobs from Berea sandstone samples.
- 4) Visualization of the state of residual oil in water-wet and transparent 2-D glass micromodels, and size distribution of

oil blobs obtained from photographs of the micromodels at residual oil conditions. The fluid pair in these experiments was dyed Soltrol oil and 2% NaCl brine.

Three kinds of analysis were performed on the solidified oil blobs collected from a given sample: 1) visual examinations of residual oil blobs under the microscope and photomicrographs of blobs, 2) photomicrographic analysis of a representative number of oil blobs by use of an image analyzer computer for obtaining the blob-size distribution of a given sample based on the projected blob perimeter and the projected blob-area distributions respectively, and 3) particle analysis of residual oil blobs of a given sample by the Coulter Counter method.

Visual examination of blobs under the microscope provided a qualitative picture of the pore structures where oil was trapped and also information about the typical capillary structures of residual oil encountered. Furthermore, visual examination of blobs provided semiquantitative information about the wetting conditions. Scanning electron photomicrographs of typical oil blobs from a given sample provided details such as the absolute size of relatively large blobs and the relatively small blobs, respectively, as well as a qualitative picture of the wetting behavior.

The residual oil blob-size analyses by the image analyzer (Quantimet) and the Coulter Counter method were aimed at obtaining blob-size distribution and the effect of capillary number on blob-size distribution.

Experimental Results and Discussion

a) Sandstone and Carbonate Core Samples

Displacement experiments using the styrene monomer-2% CaCl_2 brine fluid pair under water-wet conditions were performed in various Berea sandstone samples, in a Boise sandstone sample, and in carbonate core samples. Table 4.1 summarizes the core sample properties and flow conditions used in displacement experiments aimed at determining the effect of displacement conditions (characterized by capillary number) on the oil blob-size distribution. Data on the amount of trapped styrene in a given sample and the recovery of oil as solidified blobs from the samples are also given in Table 4.1.

The capillary number values in these experiments were varied in the range of 1.1×10^{-6} to 9.3×10^{-4} . Residual oil saturations were determined from the weight of polymerized blobs in the sample. Depending on capillary number conditions, the residual oil saturation for 16 Berea sandstone samples varied between 36.3% to 11.0% in these displacement tests. The residual oil saturations corresponding to the capillary number conditions listed in Table 4.1 are in very good agreement with capillary number displacement experiments run with the fluid pair Soltrol oil-2% CaCl_2 brine reported elsewhere.^{4.6,4.7} Furthermore, the relative

permeability values at residual oil conditions given in Table 4.1 are also in good agreement with results obtained with the Soltrol oil-2% CaCl_2 brine system, indicating that the displacement experiments were run under strongly water-wet conditions.

Inspection of solidified oil blobs by microscope revealed that the residual styrene was trapped under water-wet conditions, with residual oil blobs being of various kinds and sizes. It is convenient to classify shapes of oil blobs found in sandstone and carbonate samples as singlet, doublet and branched. Singlet blobs occupy one pore body and have a size distribution consistent with the range of pore-body sizes encountered in a given sample. For Berea sandstone, singlet blobs found at low capillary number conditions fall in the size range of 30 μm to 200 μm which corresponds to the pore-body sizes found in pore casts of Berea sandstone. Blobs involving two pore bodies connected by a liquid bridge are called doublets. Blobs of this shape commonly range from 100 μm to 400 μm in length. Branched blobs involve three or more pore bodies. They range from 150 μm to 1000 μm in length and are more frequent at low capillary number conditions.

Fig. 4.1 shows typically large oil blobs found in Berea sandstone samples. It is clear from their appearance that these blobs were trapped under water-wet conditions and that large oil blobs involve several pores and are generally branched. The lengths of these blobs range from about 400 μm to 800 μm .

The capillary structures of residual oil blobs shown in Fig. 4.1 indicate evidence of high aspect ratio. The narrow constrictions (pore throats) vary in size from 10 μm to 30 μm , whereas pore-body sizes vary from about 30 μm to 200 μm . The length of pore constrictions appears to be about twice the pore-throat diameter. Based on a relatively large collection of photomicrographs of blobs (i.e., about 10 for each Berea sample in Table 4.1), the ratio of pore-body sizes to pore-throat sizes of branch-type blobs ranged from 1.5 to as high as 10, with most frequent values of aspect ratio falling between 2.5 and 4.0.

Even though Berea sandstone usually retains a high residual oil saturation ($S_{\text{or}}^* \approx 35\%$), most of the number population of oil blobs trapped in Berea sandstone occur as singlet and doublet structures. This behavior is considered to be typical of pore networks that have high aspect ratio and was also obtained for micromodels having high aspect ratio.^{4.8}

Blobs of residual oil at low capillary number in the Boise sandstone sample were similar to those of the Berea samples, the only difference being the absolute size of blobs. The change in absolute sizes was consistent with the Boise sandstone having relatively larger pore body sizes than the Berea sandstone.

Inspection by microscope of oil blobs for conditions giving reduced residual saturations in Berea sandstone samples (i.e., Berea samples 6, 15, B-F, and D04 in Table 4.1) shows there is an increase of relatively small blobs in relation to the number of large blobs. Branched-type blobs

are still encountered after mobilization at high capillary number. The fact that not all of the relatively large blobs of oil are mobilized at capillary number conditions higher than the critical capillary number for mobilization of large blobs is not surprising. Large oil blobs may not always be exposed to high pressure gradients, because of blocking of surrounding pathways by singlet blobs that cannot be mobilized at the prevailing conditions. An interesting observation on the population of blobs after high capillary number displacement is that spherical blobs of sizes less than 50 μm are found. Fig. 4.2 shows such sub-singlet or oil droplet sizes in 3 SEM micrographs. These droplets of oil are a small fraction of the remaining reduced residual oil (e.g., less than 5% of S_{or}). However, they indicate that in the process of mobilization, some of the oil breaks up into smaller blobs, some of which have sizes smaller than the pore-throat dimensions in the medium. This result indicates that at high capillary number displacements, emulsification of residual oil and entrainment of oil droplets through the sample may be important mechanisms for oil recovery. The phenomenon of oil blobs breaking up and coalescing during mobilization has been given considerable attention in literature.^{4.9,4.10} However, the breakup of blobs into sizes much smaller than the pore dimensions has not been considered in previous considerations of blob mechanics. Visualization experiments in micromodels show that at high capillary number, mobilized blobs of oil do partially break down into sub-blobs of sizes less than those of the pore throats in the system. As such, in the process of motion, droplets were observed to collect in pore bodies without coalescing to give a cluster of sub-singlet blobs having much the same overall form and properties of an equivalent (in size) single blob. This behavior is in some ways analogous to transport of fine particles through porous media.

Fig. 4.3 shows SEM photomicrographs of oil blobs in a 40 md carbonate core sample. From these capillary structures, it appears that the residual oil was trapped under water-wet conditions. The structures of the blobs from the carbonate rock sample differed somewhat from those found in Berea sandstone (i.e., Figs. 4.1 and 4.2). The pore bodies are more irregular in the carbonate sample, as a result of the crystal-like grain structures. Branch-type blobs were more numerous in the carbonate rock than for the Berea sandstone.

b) Size Distribution of Oil Blobs in Sandstones

Determination of size distribution for irregularly shaped structures such as those shown in Figs. 4.1 and 4.3 is not a straightforward problem in particle analysis. Among the various techniques of particle size analysis, two main methods of analysis have been chosen: a photomicrographic method of analysis of images and the Coulter Counter method.

In the photomicrographic analysis of blob-size distribution, samples of blobs from a given core sample are dispersed on a microscope slide. The population of blobs under the microscope was scanned with the aid of an image analyzing system, known commercially as "Quantimet." More than

2000 blobs from a given sample were analyzed and classified in terms of both projected blob perimeter and projected blob area. The number distribution of projected blob perimeters and projected blob areas can be converted to a number distribution of equivalent blob diameters, D_{bp} and D_{ba} , given by the diameter of a circle, having the same perimeter and area, respectively, as that measured for the blob. Hence, a number distribution is obtained according to the two-dimensional features of blobs: namely, their projected perimeter and their projected area, respectively.

In the Coulter Counter method, the blobs are classified by size according to their volume. An equivalent blob diameter is obtained for blobs that have the same volume by way of assuming the diameter of a spherical particle having the same volume. Monosize spheres of accurately known diameter are used to calibrate the instrument. The Coulter Counter method is now being applied in our laboratory.

To date, only a few blob samples collected from the core samples listed in Table 4.1 have been analyzed for blob-size distributions by Coulter Counter or image analysis. Photomicrographic analysis of blob-size distribution has been performed on the blobs of Berea samples 1, 2, 6, and 8 listed in Table 4.1. Fig. 4.4 shows the number-based, blob-size distributions for Berea-1 given by projected blob perimeters and areas, respectively. Note that distributions of the two types of equivalent blob-size diameters are not the same, particularly at large blob sizes. This is because objects with the same projected perimeter can have different projected areas, and vice-versa; perimeter lengths of branched blobs will obviously give equivalent blob diameters which are higher than those for projected areas.

An interesting feature of the blob-size distributions shown in Fig. 4.4 is that 50% of blob sizes fall in the range of 30 μm to 120 μm . These sizes are consistent with pore sizes measured from SEM micrographs of resin pore casts for a Berea sandstone having properties to those of the Berea-6 sample. From published data^{4,11} on the complete photomicrographic distribution of pore sizes for another comparable Berea sandstone, 80% of the total pore volume is made up of pores in the size range of 30 μm to 120 μm . These results indicate that the majority of the blobs in Berea sandstone occupy single pore bodies (even for low capillary number displacements). Based on displacement experiments run in micromodels,^{4,8} from which it was concluded that blob-size distribution can be dominated by aspect ratio, it appears that the pore network in Berea sandstone involves pores of high aspect ratio, which cause extensive trapping of singlet blobs by the snap-off mechanism. As can be seen from Fig. 4.4(b), blob sizes greater than 300 μm (these will be mainly branched) make up about 5% of the blob population.

Fig. 4.5 shows equivalent blob sizes by perimeter distributions for the Berea-8 sample. The blob-size distribution for Berea-8, for blob sizes greater than 50 μm , compares well with that for Berea-1. This was as anticipated, both samples having been waterflooded at capillary numbers of the order of 10^{-6} . There are some minor differences in the blob

distributions for the aforementioned samples in the blob sizes smaller than 50 μm , whereby more blobs are found in this size range for Berea-8 than for Berea-1. However, when one considers the volume contribution of small blobs to the total residual oil saturation, the difference in the two distributions is fairly minor.

Fig. 4.6 shows blob-size distributions by perimeter for the Berea-6 sample where residual oil trapped at low capillary number (2.98×10^{-6}) was subsequently partly mobilized at higher capillary number (1.73×10^{-4}). It can be seen from Fig. 4.6, in comparison with results in Figs. 4.4 and 4.5, that the blob-size distribution becomes bimodal after mobilization of normal waterflood residual oil. There is, on one hand, a relative decrease in the size of large blobs in the Berea-6 sample in comparison to the blob sizes in Berea-1 or in Berea-8. On the other hand, there is significant increase in the number of relatively small blobs (i.e., blobs smaller than 50 μm). This experimental result is consistent with the notion that oil blobs, in the process of mobilization, break up into smaller blobs that remain trapped in the medium.

Fig. 4.7 provides a comparison of the number-based, cumulative distributions of blob sizes in the samples Berea-1, Berea-6, and Berea-8. Note that there are significant differences between the blob sizes obtained after high-capillary-number mobilization of residual oil (Berea-6) and those given by normal waterflood residual oil conditions (Berea-1 and Berea-8). Comparable change in blob-size distribution with capillary number was also observed in mobilization experiments run in micromodels.

Characterization of residual oil blobs by volume, based on the number distributions given in Figs. 4.4-4.7, involves somewhat arbitrary assumptions about blob shape. Because blob shape depends strongly on blob size and because the pore-body sizes as well as the pore-throat sizes do not have a narrow distribution, a realistic volume distribution, in terms of say, equivalent blob diameter by perimeter, would be difficult to justify. A possible alternative to obtaining volume-based distributions is through particle analysis by the Coulter Counter technique.

Blob samples of Berea-12, 14, and 15 samples listed in Table 4.1 were analyzed by another laboratory (Coulter Electronics, Inc.) using the Coulter Counter technique. Results of blob-size distributions by volume for the aforementioned samples are shown in Fig. 4.8(a). It can be seen that the results of blob-size distributions in Fig. 4.8(a) do not demonstrate clearly the effect of capillary number on blob-size distribution. It is suspected that the main reason for this behavior is in sampling from the blob population sent for analysis. Recently, a Coulter Counter apparatus was installed in our laboratory. The aforementioned samples have been reanalyzed, and the results are shown in Fig. 4.8(b). It can be seen that our analysis of blob samples differs from the results shown in Fig. 4.8(a). Furthermore, the results of blob-size distribution shown in Fig. 4.8(b) show the anticipated trend in blob-size distribution with increased capillary number conditions. At increased capillary number conditions, there is a shift towards smaller

size blobs. For example, blobs of size $D_{bv} < 200 \mu\text{m}$ in Berea-12 sample make up 40% of the residual oil saturation, whereas the blobs of size $D_{bv} < 200 \mu\text{m}$ in samples Berea-14 and Berea-15 make up 80% of the residual oil saturation at the capillary number conditions indicated in Fig. 4.8(b).

The blob-size distribution for Berea-15 sample shows the occurrence of relatively smaller size blobs to be greater than was observed for sample Berea-12. For example, blobs of size $D_{bv} < 80 \mu\text{m}$ make up only 2% of the value of S_{or} in Berea-12, while in Berea-15 blobs of size $D_{bv} < 80 \mu\text{m}$ make up 18% of the value of S_{or} . Taking into account that the residual oil saturation values for Berea-12 and Berea-15 were 30.7% and 13.0% respectively, the blob-size distributions show that at increased capillary number conditions, additional small blobs are obtained as a result of breakup of blobs into singlets and sub-singlets during the process of mobilization. This mechanism is consistent with observations of mobilization in micromodels. However, it differs from mechanisms of mobilization of residual oil used in the modelling of residual oil saturation as a function of capillary number.^{4.12} The theoretical treatments of oil-blob mechanics during mobilization^{4.8,4.9} appears to be qualitatively correct with respect to the mechanism of breakup of blobs. We have yet to test how well the theoretical treatment of blob mechanics fits with experimental results, such as those shown in Fig. 4.8(b).

The results of Coulter Counter analysis are very reproducible for blobs of a given sample. The reproducibility of blob analysis is shown in Fig. 4.9 for repeated analyses run in our laboratory for blobs of Berea-15 sample. It can be seen that results are highly reproducible for blob populations in excess of 15,000.

Using the Coulter Counter method, we anticipate the analysis of all blob samples from the core samples listed in Table 4.1. This should enable more definitive evaluation of the effect of capillary number on blob-size distribution for residual oil saturations in the range of 35% down to 13%.

c) Residual Oil Structure in Bead Packs

Low capillary-number-displacement experiments have been performed in unconsolidated 35-40 mesh packings of glass beads using styrene monomer as the nonwetting phase. Typical capillary structures under strongly wet conditions are shown by the photographs in Fig. 4.10. Oil blobs occupying 1 to 4 pore bodies are clearly illustrated in Fig. 4.10(a) and (b). Relatively large blobs found in bead packs are shown in Fig. 4.10(c) and (d). The relatively large blobs involve 7 to as much as 30 pore bodies. It has been reported^{4.5} that the normal waterflood residual oil in bead packings consists of: singlet blobs of size 1 pore body (65% of the number of blobs), blobs of 2 pore bodies (20% of the number of blobs), and branched-type blobs for the remainder. Classification of blobs obtained in our laboratory in accordance with this scheme has shown 59% of the blobs were singlets, 17% were doublets, 8% were triplets, and the remaining 16% were blobs involving 4 to 30 pore bodies that are usually

branched-type. These results are in very good agreement with the results of past work.^{4.5}

The complete number-based and the approximated volume-based distribution of blobs in bead packs is shown in Fig. 4.11. The volume-based distribution was obtained from the number-based distribution by assuming pore throats and pore bodies to be equal in volume. Thus, a blob of size 2 has 3 times the volume of a singlet blob, a blob of size 3 has 5 times the volume of a singlet, a blob of size 4 has 7 times the volume of a singlet, and so on. By sieving the blobs, it was found that blobs greater than 840 μm (blobs greater than about 9 pore bodies) made up 44% of the residual oil volume, while blobs in the size range 200-840 μm (1 to 9 pore bodies) made up 56% of the residual oil volume. The approximated volume distribution of blobs shown in Fig. 4.11 is consistent with this independently measured quantity. From Fig. 4.11, it is seen that blobs of size 9 pore bodies and larger make up 46% of the residual oil volume.

d) Structure of Residual Oil in Micromodels

The effects of pore structure on the magnitude of residual oil and its detailed structure at waterflood conditions have been studied in a large variety of 2-D pore networks of various geometries. Results of this study have been presented and discussed at length elsewhere.^{4.8} A condensed version of this study is presented here.

Fig. 4.12(a) shows residual oil structures in a square lattice-type model with size distribution of pore bodies and pore throats. It is noted that the capillary structures of residual oil are determined by the arrangement of pores in the parent network. Trapping occurs as singlets in pore bodies of high aspect ratio. Branched-type blobs are found in the relatively large pore bodies surrounded by smaller pores. In the brick lattice-type network model shown in Fig. 4.12(b), residual oil is trapped in a larger fraction of pore bodies as a result of higher aspect ratio. Furthermore, the relative size of large blobs in the model shown in Fig. 4.12(b) is smaller than the size of large blobs in the model shown in Fig. 4.12(a). This is the result of high aspect ratio which causes oil to be trapped by the snap-off mechanism.

Fig. 4.13(a) shows the residual oil structures in a random pore geometry system where the aspect ratio is not very high. As a result of the bypassing mechanism, oil gets trapped in clusters involving many pores. Fig. 4.13(b) shows the residual oil structure in a random pore geometry characterized by high aspect ratio pores. As a result of the snap-off mechanism, oil gets trapped in single pores.

Fig. 4.14(a) shows the residual oil structures in a random network with macroscopic heterogeneities, in the sense that a continuum of large pores is present. It is noted that the structure of residual oil reflects the pore geometry of the parent network. Large blobs are found in the pore spaces of the large pores that make up the heterogeneity. The structure of trapped oil in the pores that are not part of the macroscopic

heterogeneity is not affected by it. It is noted that high displacement efficiency of oil is associated with the volume of oil in pore throats.

Fig. 4.14(b) shows the residual oil structure in a model with vuggy pores. It is shown that all of the vuggy pores trap oil under water-wet conditions, and oil recovery comes from the pore-throat volume.

Size distributions of oil blobs in micromodels have been determined manually from photographs of the state of residual oil in micromodels of regular lattice geometries of the kind shown in Fig. 4.12, but of variable pore-size distribution and variable arrangement of pores. Fig. 4.15 shows the blob-size distribution for the models of Fig. 4.12 and another brick lattice-type model of smaller aspect ratio than the model shown in Fig. 4.12(b). It is noted from Fig. 4.15 that blob-size distribution is significantly affected by aspect ratio and the manner in which pores are distributed with respect to each other. The fact that a relatively larger fraction of singlet blobs were found in the square network than in the brick lattice model is due to increased pore accessibility at the microscopic level as a result of higher pore coordination. However, the effect of pore coordination number, Z , is minor in comparison to that of aspect ratio and arrangement of pores.

Conclusions

1. Experimental techniques have been developed for qualitative and quantitative characterization of residual oil blobs in sandstones, carbonates, and in micromodels of 2-D pore networks as a function of capillary number conditions.

2. The size and shape of residual oil-blob structures at normal waterflood conditions is predetermined by the pore structure of the reservoir rock. In Berea sandstone, oil blobs formed under water-wet conditions occur in the size range 30 μm to 1000 μm long, and oil blobs occupy 1 to 10 pore bodies. More than 50% of the residual oil is held in single pore bodies in the size range 100 μm to 200 μm .

3. From visualizations in micromodels, the blob-size distribution is affected by pore-size distribution, but more importantly the manner in which pores are distributed with respect to each other.

4. If the aspect ratio of the pore network of the medium is high, oil blobs are trapped as singlets. The blob-size distributions of Berea sandstone imply that Berea sandstone has high aspect ratio and no macroscopic heterogeneities.

5. During mobilization of residual oil, oil blobs break up to sub-blobs, with a significant fraction of locally mobilized oil blobs retained in the medium. This phenomenon leads to narrower blob-size distribution at high capillary number displacements.

References

- 4.1 Melrose, J. C. and Brandner, C. F., "Role of Capillary Force in Determining Microscopic Displacement Efficiency for Oil Recovery by Water Flooding," J. Can. Pet. Tech. 13 (1974) 42.
- 4.2 Ng, K. M., Davis, H. T., and Scriven, L. E., "Visualization of Blob Mechanics in Flow Through Porous Media," Chem. Eng. Sci. 33 (1977) 1009.
- 4.3 Morrow, N. R., "Interplay of Capillary, Viscous and Buoyancy Forces in the Mobilization of Residual Oil," J. Can. Pet. Tech. 18 (1979) 35.
- 4.4 Craze, R. C., "Performance of Limestone Reservoirs," Trans. AIME 189 (1950) 287.
- 4.5 Robinson, R. L. and Haring, R. E., "Experimental Study of Residual Oil Configuration in Unconsolidated Sand," Jersey Production Research Company Report, Production Div., Jan. 1962.
- 4.6 Morrow, N. R. and Chatzis, I., "Measurement and Correlation of Conditions for Entrapment and Mobilization of Residual Oil," Final Report to the U.S. Department of Energy, Report No. DOE/BETC/3251-12 (Oct. 1981).
- 4.7 Chatzis, I. and Morrow, N. R., "Capillary Number Relationships for Sandstones," SPE 10114, presented at SPE 56th Annual Fall Meeting of SPE of AIME, San Antonio, Oct. 5-7, 1981.
- 4.8 Chatzis, I., Morrow, N. R., and Lim, H. T., "Magnitude and Detailed Structure of Residual Oil Saturation," SPE 10681, presented at the Third SPE/DOE Joint Symposium on Enhanced Oil Recovery, Tulsa, April 4-7, 1982.
- 4.9 Ng, K. M. and Payatakes, A. C., "Stochastic Simulation of the Motion, Breakup and Stranding of Oil Ganglia in Water-Wet Granular Porous Media During Immiscible Displacement," AIChE J. 26 (1980) 419.
- 4.10 Payatakes, A. C., Ng, K. M., and Flumerfelt, R. W., "Oil Ganglion Dynamics During Immiscible Displacement: Model Formulation," AIChE J. 26 (1980) 430.
- 4.11 Dullien, F. A. L. and Dhawan, G. K., "Characterization of Pore Structure by a Combination of Quantitative Photomicrography and Mercury Porosimetry," J. Coll. Int. Sci. 47 (1974) 337.
- 4.12 Larson, R. G., Davis, H. T., and Scriven, L. E., "Displacement of Residual Nonwetting Fluid from Porous Media," Chem. Eng. Sci. 36 (1981).

Table 4.1 Cores and Flow Conditions used in Experiments on Blob Size Distributions

Core Sample	Sample Properties				Waterflooding Data			Polymerization Data		
	ϕ (%)	K_a (md)	K_w (md)	Pore Volume (cm ³)	S_{or} (%)	K_{rw}	$\frac{K_w \Delta P}{L \sigma}$	Weight of blobs in sample	Weight of blobs collected after leaching	% Recovery of blobs
Berea-1	21.26	884	269	12.40	28.2	0.173	6.45×10^{-6}	3.18 g.	2.85 g.	89.6
Berea-2	21.58	977	312	12.24	31.0	0.126	1.54×10^{-5}	3.45	1.85 [†]	--
Berea-6	20.76	1014	507	12.46	-- 13.2	0.296 0.605	2.98×10^{-6} 1.73×10^{-4}	-- 1.48	-- 1.75 ^{††}	--
Berea-7	20.72	716	276	15.2	-- 23.8	0.135 0.178	5.26×10^{-6} 3.42×10^{-5}	3.29	3.2	97.2
Berea-8	20.56	696	243	12.25	27.2	0.299	1.1×10^{-6}	2.43	2.45	100.0
Berea-9	17.84	248	184	12.20	28.9	0.265	6.51×10^{-5}	--	1.90 [†]	--
Berea-10	17.44	240	173	12.26	29.5	0.218	5.93×10^{-5}	3.29	2.10 [†]	--
Berea-11	19.35	465	322	4.99	29.5	0.197	2.79×10^{-6}	1.34	1.04	77.6
Berea-12	19.36	937	619	11.74	-- 30.7	0.175 0.245	1.06×10^{-5} 9.36×10^{-5}	3.28	2.61	79.6
Berea-13	20.08	881	518	11.25	-- 26.0	0.193 0.492	3.2×10^{-6} 2.08×10^{-4}	2.05	2.02	97.6
Berea-14	20.60	840	505	10.82	--	--	3.4×10^{-4}	--	1.9	--
Berea-15	21.60	642	361	7.05	-- 13.0	0.217 0.92	5.6×10^{-6} 5.74×10^{-4}	1.00	0.81	81.0
Berea-B-F	18.53	957	790	10.30	-- 11.0	0.085 0.505	-- 9.3×10^{-4}	1.03	0.77	74.8
Berea-D01	18.58	142	116	12.05	36.3	0.095	7.45×10^{-6}	3.98	3.56	89.4
Berea-D03	19.63	343	295	7.97	-- 18.3	0.043 0.241	2.51×10^{-6} 3.76×10^{-4}	1.32	1.08	81.8
Berea-D04	20.60	671	294	10.82	-- 18.3	0.111 0.781	2.3×10^{-6} 4.6×10^{-4}	1.80	1.44	80.0
Boise	25.72	2090	690	19.2	27.9	--	1.82×10^{-6}	4.88	3.80	77.9
Carbonate-2	19.22	75	41.1	3.08	-- 44*	0.227 0.261	3.63×10^{-6} 1.47×10^{-5}	1.18	0.560	47.5
Carbonate-3	19.60	75	41.0	1.59	-- 47*	0.150 0.438	6.95×10^{-6} 2.78×10^{-5}	0.69	0.430	62.2
Carbonate-4	19.60	75	38.7	2.06	-- 39*	0.153 0.410	3.13×10^{-6} 4.7×10^{-5}	0.73	0.417	57.1

[†] Only part of the rock sample was leached by HF acid

^{††} Particulates of rock material along with the blobs

*Values are for small samples and are approximate

FIGURE 4.1. RELATIVELY LARGE BLOBS FOUND IN BEREA SANDSTONE SAMPLES.

FIGURE 4.2. EXAMPLES OF SINGLET BLOBS FROM BEREA B-F SANDSTONE SAMPLE. (SEE TABLE 4.1).

FIGURE 4.3. TYPICALLY LARGE BLOBS AND SMALL BLOBS FROM CARBONATE CORE SAMPLES.

FIGURE 4.4. PHOTOMICROGRAPHIC BLOB-SIZE DISTRIBUTIONS FOR THE BEREIA-1 SANDSTONE SAMPLE.

FIGURE 4.5. PHOTOMICROGRAPHIC BLOB-SIZE DISTRIBUTION FROM PROJECTED PERIMETER FOR BEREА-8 SANDSTONE SAMPLE.

FIGURE 4-6. PHOTOMICROGRAPHIC BLOB-SIZE DISTRIBUTION FROM PROJECTED PERIMETER FOR BEREA-6 SANDSTONE SAMPLE.

FIGURE 4.7. THE EFFECT OF CAPILLARY NUMBER ON BLOB-SIZE DISTRIBUTION.

(a) ANALYSIS PERFORMED BY COULTER ELECTRONICS.

(b) ANALYSIS PERFORMED IN OUR LABORATORY.

FIGURE 4.8. VOLUME-BASED BLOB-SIZE DISTRIBUTIONS FOR BERE 12, 14, 15 SAMPLES OBTAINED BY INDEPENDENT MEASUREMENTS. (COULTER COUNTER.)

FIGURE 4.9. REPRODUCIBILITY OF VOLUME-BASED DISTRIBUTIONS OF OIL BLOBS (COULTER COUNTER).

FIGURE 4·10. TYPICAL OIL-BLOB STRUCTURES FORMED IN RANDOM PACKINGS OF 35-40 MESH BEADS.

FIGURE 4.11. DIMENSIONLESS NUMBER-BASED AND VOLUME-BASED DISTRIBUTIONS OF BLOBS FOR 35-40 MESH PACKINGS OF GLASS BEADS (low capillary number).

(a) PATTERN WITH
 $Z=4$

MODEL NO. SQ-L-1

1 cm.

(b) PATTERN WITH
 $Z=3$

1 cm.

MODEL NO. HH-L-1

FIGURE 4.12. EFFECTS OF PORE-SIZE DISTRIBUTION AND COORDINATION NUMBER ON OIL TRAPPING.

FIGURE 4.13. OIL-BLOB STRUCTURES IN TWO MODELS WITH RANDOM PORE INTERCONNECTIONS.

FIGURE 4.14. DISTRIBUTION OF RESIDUAL OIL IN TWO MICROMODELS WITH RANDOM INTERCONNECTIONS AND MACROSCOPIC HETEROGENEITIES.

FIGURE 4.15. BLOB-SIZE DISTRIBUTIONS IN MICROMODELS.

RESEARCH AND CORRELATION OF CONDITIONS
FOR ENTRAPMENT AND MOBILIZATION OF RESIDUAL
OIL

DOE/BC/10310-20

NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY (CROCKER)

TITLE PAGE	CONTEXT 3	FIGURE 5	EXPERIMENTAL TASK 1	TABLE 3	REFERENCE	TABLE 11.2	TABLE 11.5	TABLE 12
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33. FIG. 3.8	34. TASK 4	35. TASK 5	36. EXPERIMENTAL	37. TABLE 3.10	38. TABLE 3.10	39. TABLE 3.10	40. TABLE 3.10	41. TABLE 3.10
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