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Application of Capillary Pressure Measurements to the Determination of Connate Water Saturation

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I. INTRODUCTION

This chapter is concerned with the physics of capillarity as it relates to the retention of connate water both in oil and gas reservoirs and in laboratory environments. The determination of the reservoir average value of the connate water saturation is a major factor in the evaluation of the total original-oil-in-place. As such, this average saturation value can in some circumstances be of considerable economic significance. Understanding the physics of capillarity is clearly of critical importance in interpreting and evaluating such data.

The purpose of the present discussion is to focus attention on some early, as well as recent, studies that have to do with a particular feature of the overall problem of determining connate water saturation, namely, the interpretation of capillary pressure measurements. This feature has not been given sufficient attention in the past. Thus, our purpose is not simply to recapitulate or summarize the existing extensive literature on the general subject of connate water. It is, rather, to reexamine the usual assumption that the connate water saturation is a parameter that can be easily and satisfactorily determined by any one of several different conventional approaches.

One of the most frequently used of these approaches involves the experimental determination of drainage capillary pressure curves. As with all methodologies based on core samples, it is assumed that a representative set of such samples is available. It is also assumed that the resulting set of drainage capillary pressure curves can be correlated with some other suitable set of core property data, so as to lead eventually to the construction of an appropriate reservoir average water saturation versus capillary pressure curve. Aside from these sampling and averaging assumptions, it is usually taken for granted that no further problems arise in applying experimental capillary pressure data. It is this uncritical use of conventionally obtained capillary pressure curves that we wish to review and discuss in detail.

In most of the early literature in which capillary pressure data on reservoir core samples are reported, the measured water saturation appears to approach a minimum value with increase in capillary pressure. Great significance has been attached to this saturation value, and it has been commonly, but we believe erroneously, assumed to be an equilibrium value, corresponding to the saturation given by hydrostatic equilibrium in the reservoir. Thus, the laboratory-determined minimum wetting-phase saturation has been regarded

as characterizing the connate water saturation even at large distances above the oil-water contact. A further consequence has been that the terms irreducible minimum water saturation (or irreducible saturation) and connate water are now often used synonymously. Also, water retained by core samples and other forms of porous media as a result of some form of laboratory displacement experiment often serves as a model for reservoir connate water. However, the methods used to achieve some initial level of water saturation can often be sufficiently different to make this initial value almost arbitrary. Furthermore, this initial water saturation can have a dominant influence on the outcome of the experiment.

Methods of establishing an initial water saturation, or selecting a value to aim for, include the aforementioned capillary pressure measurements. Such methods also include flooding with oil at some selected viscosity and pressure gradient, measurement of the reservoir water saturation from electric logs by coring, and, finally, determination of the saturation level achieved by somewhat arbitrary mercury injection pressures or centrifuging conditions. Usually, little attention is given to whether such saturations and associated surface curvatures correspond to capillary equilibrium. In fact, the existence of a well-defined irreducible saturation is probably a strong indication that the capillary pressure at the water-oil or water-gas interface is actually less than the value indicated by the method of measurement. Asserting that this value applies to the reservoir implies that the reservoir does not achieve capillary equilibrium even after geologic time. In this context, one of the early observations that is most difficult to explain is that water saturations in re-covered core samples appear to be in fair agreement with irreducible saturations measured in capillary pressure tests. These observations are summarized in a later section of this chapter.

The general practice of using the term irreducible minimum saturation indiscriminately to describe almost any kind of low water saturation has caused confusion. More importantly, the implied assumption that a minimum wetting-phase saturation exists in the reservoir is unwarranted. It appears that the assumption that irreducible saturations are equilibrium values can lead to serious errors in both the measurement and interpretation of capillary pressure curves. Results from early soil science literature and recently reported experimental evidence that support this point of view will also be discussed below.

II. DISCOVERY OF INTERSTITIAL WATER

The existence of connate water in zones that produce clean oil was not readily accepted in the early days of petroleum engineering. An interesting review by Torrey [1] provides early references to the

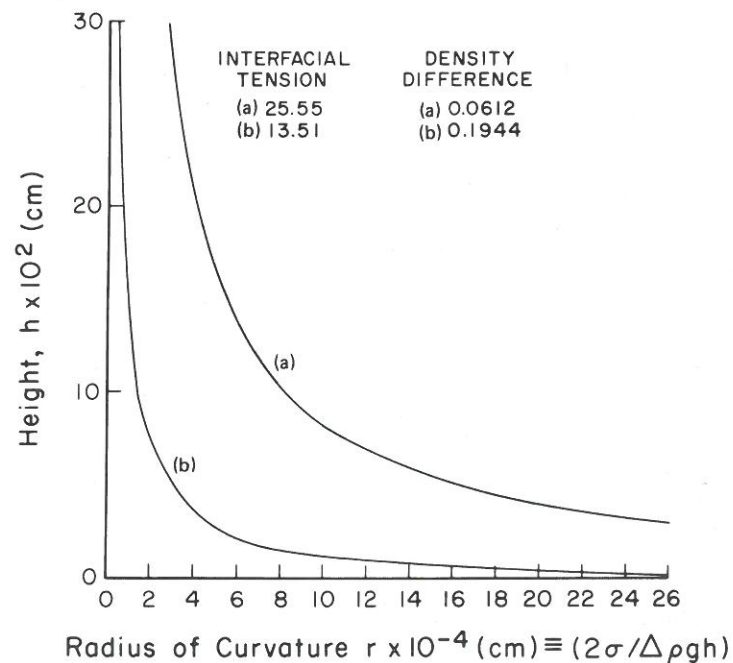


FIG. 1 Height versus mean radius of curvature of interface for connate water in equilibrium with the free water surface. (Note that if an interface exists, its curvature at any height depends on interfacial tension and density difference, but is independent of wettability.) (After Ref. 3.)

subject. Schilthuis [2] provided conclusive evidence of the presence of connate water by analysis of cores cut with an oil base mud of extremely low water content. It also became clear that electric logging measurements depended on the presence of connate water. A theoretical reason for the presence of connate water in terms of a balance between hydrostatic and capillary forces was first given by Garrison [3]. A plot of height above the free water surface versus radius of oil-water interface curvature is shown in Fig. 1. Garrison's theory accompanies virtually every discussion of connate water distribution. However, from previous discussions [4, 5] and the following review, it will be seen that there are aspects of its application to capillary equilibrium and the interpretation of capillary pressure curves that are much less firmly established than is generally assumed.

III. PHYSICS OF CAPILLARITY

For present purposes the term "physics of capillarity" will be taken to mean the thermodynamic conditions for equilibrium that apply to fluid-fluid and fluid-solid interfaces at the microscopic or sub-pore-size level. These conditions are usually regarded as well known, and useful treatments may be found in many standard texts in mathematics, physics, and chemistry. The application of these conditions to reservoir problems, however, sometimes involves subtle features not adequately treated in the more elementary texts. These features have been pointed out in previous discussions by the present authors [6, 7, 8, 9, 10]. Only a brief summary of the physics of capillarity is therefore given here.

For immiscible fluids held within the pores of reservoir rocks, the fluid-fluid interfaces are highly curved unless the wetting state of the pore surfaces happens to be of an exactly neutral character. These curvatures govern the differences in pressure between the various fluids occupying an individual pore or a pair of adjoining and communicating pores. The fundamental relationship between the pressure difference for a given fluid pair P_c , called the capillary pressure, and the interface curvature J is given by the Young-Laplace equation.

$$P_c = \gamma J \quad (1)$$

Here, γ denotes either the surface tension of a gas-liquid interface or the interfacial tension of a liquid-liquid interface. Equation (1) may be called the first condition for equilibrium. Although the stability of an interface depends on appropriate boundary conditions, it should be emphasized that neither the magnitude of γ nor the applicability of Eq. (1) itself depends on the chemical nature or the configuration of the solid surface. The equilibrium configuration corresponding to Eq. (1) is established very quickly. Equation (1) governs only the interrelationship between fluid interface curvatures and the corresponding capillary pressures. For fluids of matched density, the shape of each fluid interface is such that the curvature J is the same at all points on the interface. Changes in curvature caused by difference in fluid densities are generally negligible at the microscopic (pore scale) level. The condition of constant curvature does not, of course, imply that such shapes are spherical in form.

In applying Eq. (1) to calculations of surface curvatures at equilibrium, a second condition of thermodynamic equilibrium relating to the boundaries of an interface is also taken into account. This condition, known as the Young equation, can be written as a relationship among the three interfacial tensions of the immediate

neighborhood of a three-phase contact line at a smooth solid surface. Young's equation involves the contact angle θ made by the fluid-fluid interface at the solid surface. This contact angle, defined as the angle measured through one of the two fluid phases, is thus determined only by the three tensions involved. Detailed discussions of the thermodynamic properties of surface films and their effect on contact angle are given in Chapters 2 and 3. In practice, surface roughness, edge effects, and heterogeneity in surface wetting properties can all contribute to boundary conditions that cannot be described by a unique contact angle. Given the complexity in mineralogy and pore structure of reservoir rock pore surfaces, and rock/crude oil/brine interactions, any attempt to characterize reservoir wettability by a single contact angle obviously requires careful qualification.

In spite of these complexities, a definitive discussion of many aspects of the physics of capillarity requires only a single value of the contact angle. For a given pore geometry and single-valued contact angle, the two conditions of equilibrium can be used to determine the curvature at which pores can be entered by a displacing fluid. Stability conditions for fluid-fluid interface shape or configuration are also involved [11]. Generally, in reservoir rocks, two adjoining pores can be described as having pore walls that are alternately converging and diverging so that the two pore bodies are linked by a pore throat. There will then be a limited range of stable configurations of differing interface curvature within an individual pore body and its associated throats. This range of configurations will be characterized by maximum and minimum values of the interface curvature. This then gives rise to hysteresis in the relationship between capillary pressure and saturation [7, 9, 10, 12].

IV. SATURATION AND PORE SIZE DISTRIBUTION

Relationships between capillary pressure and saturation (the capillary pressure curve) are determined by interconnected assemblies of pores and are thus strongly dependent on the overall distribution of pore sizes and on local variations in pore size distribution within a rock sample. Detailed discussion of this dependency based on analysis of network models is presented in Chapter 4 of this book. The maximum and minimum values of the interface curvature, mentioned previously, correspond to the types of displacement that can take place within an individual pore. These are drainage (maximum stable curvature) and imbibition (minimum stable curvature). Thus, even when a strongly wetting condition is maintained, time-independent hysteresis is a characteristic feature of a true (rather than apparent) equilibrium capillary pressure curve. Changes in wetting conditions produce large changes in this type of hysteresis [13].

Although the measurement of saturation is elementary, the concept becomes much more complex when considering an assemblage of individual pores either fully or partially occupied by one of the fluids. For example, the measured wetting phase saturation will include contributions from (1) the pore volume of pores not yet invaded by the nonwetting phase, (2) pendular volumes trapped at the contacts between individual solid grains and other forms of retained wetting phase, (3) microporosity associated with larger pores already invaded by the nonwetting phase, and (4) adsorbed films on the surfaces of the invaded pores.

The recognition that there are a variety of contributions to the measured saturation is important when the problem of scaling capillary pressure data is considered. For example, mercury injection capillary pressure curves are measured routinely for reservoir rocks and are often assumed to provide representative drainage curves for strongly water-wet conditions. However, wetting films are absent (the wetting phase being a vacuum), and such data do not reflect this contribution to the wetting phase saturation. Thus, the mercury injection data cannot be directly scaled to a strongly wetting condition. This is, of course, primarily of concern in the low saturation range. A procedure for estimating the needed correction for mercury injection data has been proposed by Melrose [8].

A second difficulty in scaling mercury injection data also arises in the low saturation region. This difficulty has been termed the converging pore wall (CPW) effect [8]. It may be explained by considering, for example, the case of a small straight-walled capillary tube of radius R . For this particular pore shape the curvature of any fluid-fluid interface within the pore is given by the well-known expression

$$J = 2 \cos \theta / R \quad (2)$$

Since Eq. (2) is restricted to the specified pore wall configuration and since such pores do not actually occur in reservoir rocks, it follows that Eq. (2) is not, in fact, applicable to reservoir problems. The method of adjusting mercury injection data, given in most texts, assumes that Eqs. (1) and (2), taken together, can be so applied.

This error cannot be remedied simply by regarding R as the radius of an "equivalent" capillary tube because the factor $\cos \theta$ does not represent the correct dependence of curvature on θ for pore walls that are either converging or diverging. For the low saturation range the predominant pore wall configurations are of the converging type. Thus, if it is intended that mercury injection data be scaled to a strongly wetting condition, correction for the CPW effect is also required. This correction can be expressed either as an addition to the measured saturation or as an increased value of the applicable capillary pressure [8].

V. ATTAINMENT OF EQUILIBRIUM CONDITIONS

The thermodynamic conditions for equilibrium, which have been discussed above, clearly apply at the microscopic or sub-pore-size level. Whether they apply to the pore-size level or to a core plug sample as a whole depends on a number of factors. These include the initial and final states, the rates of the various transport processes involved in the approach to equilibrium, and the time allowed for equilibrium to be reached.

At low wetting-phase saturations, equilibrium requires transport out of or into pendular volumes, microporosity, and wetting films. These processes no doubt involve several types of transport. These include hydrodynamic flow in thin films and in microporous structures. The surface area associated with thin films and the quantity, size, and distribution of microporous structures within the matrix pore space then become important factors.

Other transport processes, which may well be involved, can be classified as diffusional in nature. Both surface diffusion and bulk-phase diffusion may contribute significantly to the attainment of equilibrium. Recent studies of the low saturation region of the capillary pressure curve for samples of Berea sandstone [14] and low-permeability gas sands [15], using the water-vapor desorption method, clearly involve diffusional transport in the vapor phase. The times required for reaching equilibrium were of the order of several days, weeks, or even months.

With respect to the attainment of equilibrium in the reservoir over geologic time, it seems reasonable to assume that the hydrodynamic and diffusion processes are sufficient. In this case, equilibrium must be established in response to the effect of the gravitational field on fluid phases of differing densities. Thus, the physics of capillarity operates within the context of the principles of hydrostatic equilibrium. The following section deals with the various questions that then arise with respect to application to hydrocarbon reservoirs.

VI. HYDROSTATIC EQUILIBRIUM

Application of the principles of hydrostatic equilibrium to the distribution of connate water in hydrocarbon reservoirs as first proposed by Garrison [3] was considered in more detail by Leverett [16]. It was explained that because of capillary forces there would be a transition zone between the reservoir and the underlying aquifer. Capillary pressure would increase with height h , above a hypothetical free water surface. At equilibrium the capillary pressure P_c across a curved oil-water (or gas-water) interface is given by

$$P_c = \Delta\rho gh \quad (3)$$

where $\Delta\rho$ is the density difference and g the acceleration due to gravity. Three questions (at least) arise in the application of this relationship. These are:

1. Does this theory hold above the transition zone? In most accounts of connate water it is assumed that this equation holds throughout the reservoir. Because the reservoir has geologic time for equilibration this assumption seems highly reasonable. However, there are observations relating to cores taken with oil base muds and laboratory-measured capillary pressure relationships that are difficult to reconcile with the equilibrium condition expressed by Eq. (3).
2. What is the effect of capillary pressure hysteresis? Even if capillary pressure and hence interface curvature is in accordance with Eq. (3), it cannot be assumed that the connate water saturation is determined by the curvature alone. Capillary pressure hysteresis and possible variations in wettability related to reservoir properties and history permit a wide possible range of saturations in the transition zone at a single value of curvature. In several early publications, the imbibition curve was considered to be more representative of the equilibrium that would be attained in the reservoir [16, 17, 18]. However, in subsequent practice, reservoir engineers have assumed that drainage curves for the equivalent of strongly water-wet conditions starting at 100% initial water saturation can be used to estimate connate water saturation. This is certainly a convenient (because drainage curves are more readily measurable than imbibition curves) and plausible (drainage of water accompanies accumulation of oil) assumption, but it appears to have been adopted without rebuttal of the rationale provided earlier for use of the imbibition curve. Detailed knowledge of reservoir properties and water distribution in the reservoir would be needed to resolve this neglected question.
3. What is the effect of wettability on connate water distribution? It is generally believed that oil accumulated in the reservoir trap by a drainage process under strongly water-wet conditions. Although the reservoir may not be strongly water wet at the present time, the original water distribution may be maintained because of contact angle hysteresis. Swanson [19] rationalizes the interpretation of electric logs on these grounds. However, McKellar and Wardlaw [20] recently presented novel results on microscopic fluid distribution in reservoir core samples that showed oil to be occupying at least some of the finest pores in a core cut with lease crude oil. There is also a general claim that low connate water saturations are evidence of an oil-wet reservoir. On the other hand, capillary pressure measurements for fresh reservoir cores and restored cores often show

high retention of water (see Sec. XIII on wettability). Such behavior could involve a relatively complex drainage mechanism. Thus there is a good case for keeping an open mind on the effect of wettability on water distribution and electric logging measurements.

In summary, questions that still need to be considered are:

(1) Does the equilibrium expressed by Eq. (3) hold for the reservoir both in and above the transition zone? (2) Does drainage or imbibition or some intermediate saturation condition apply to the transition zone? (3) How does the history of oil accumulation and reservoir wettability affect the distribution of connate water within a virgin reservoir and what effect does this have on logging measurements?

The present discussion will concentrate mainly on question 1. This question is important because the effect of equilibration on the amount of water held above the transition zone can have very large effects on the estimation of oil in place particularly in thick pay zones. Note that if the reservoir is at equilibrium, Eq. (3) will hold, even though saturation history and wettability may give wide possible variety in the saturation and microscopic distribution of connate water.

VII. CALCULATED EQUILIBRIUM COMPARED WITH EXPERIMENTAL CAPILLARY PRESSURE RELATIONSHIPS FOR BEAD PACKS

Water retention in bead packs provides a useful starting point for discussion of water retention because model calculations for theoretical (equilibrium) capillary pressure curves can be compared with experimental results. A classic study of water retention in bead packs was reported by Haines [12]. Key features of this work (see Fig. 2) were:

1. Capillary pressure curves for drainage and imbibition.
2. Correlation of results by the scaling group $P_c R / \sigma$, a forerunner of the Leverett [16] $j(s)$ function (here, R is the average bead radius).
3. Experimental data that feature an irreducible saturation.
4. An unequivocal explanation of loss of hydraulic contact of pendular rings at point contacts between spheres as the cause of the observed irreducible saturation.
5. Model calculations for regular sphere packings of equilibrium relationships between capillary pressure and water saturation based on the pressure-volume relationships for pendular rings at sphere-sphere contacts [21, 22, 23], packing coordination number (number of contacts per sphere), and porosity.
6. Side-by-side comparison of experimental irreducible saturations (these are nonequilibrium saturations because interface curvature

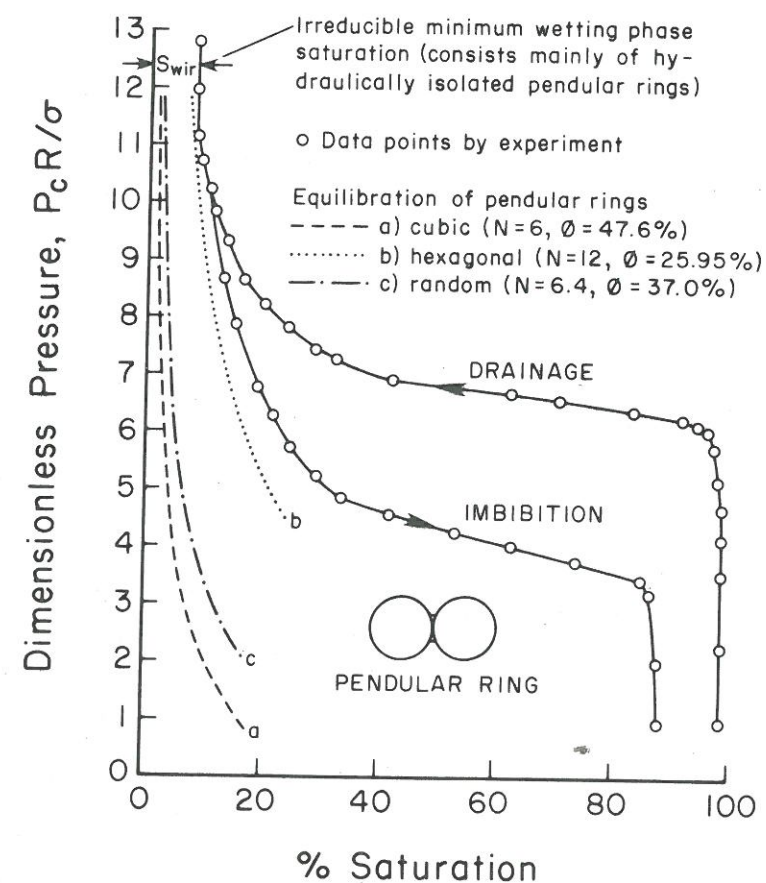


FIG. 2 Experimental and theoretical capillary pressure relationships for sphere packings. Equilibrium relationships of curvature versus saturation at low saturations can be calculated exactly for sphere packs of given coordination number N , and porosity ϕ , and can be estimated for random packings of equal spheres. In drainage experiments on smooth spheres, pendular rings and other capillary structures become disconnected at some pressure and volume related to the drainage pressure. (Equilibration via surface films at a drained solid surface or by vapor transport is extremely slow. Thus a well-defined nonequilibrium irreducible saturation is observed.) (After Ref. 12.)

no longer changes in accordance with the externally measured pressure) and calculated equilibrium capillary pressure curves, which are always much less than the irreducible saturation above pressures at which the irreducible saturation is formed.

Smith [24, 25] and Smith et al. [26] working contemporaneously with Haines reached similar conclusions. The work of Haines and Smith clearly demonstrated the differences between experimental (nonequilibrium) and theoretical (equilibrium) capillary pressure curves associated with the drastic loss of hydraulic conductivity at low water saturations. Equilibration through drained films at solid surfaces, even when completely wetted, or by equilibration through the vapor phase, can be extremely slow. This is especially true when, as in the experiments of Haines and Smith, the solid surface area is extremely low.

Subsequent accounts of capillary retention given in text books do not do justice to this early work. Keen [27] reported on Haines' work in a text entitled *The Physical Properties of the Soils*. The experimental results of Haines were presented but the form of the resulting curves was explained in terms of the equilibration of pendular rings. At the same time, in a figure showing Haines' results, the curves given by the corresponding equilibrium calculations were omitted. A similarly confused account of Haines' work, given by Dallavalle [28] in the book *Micromeritics*, appears to have come from Keen [27]. Similar misconceptions pervade the numerous discussions of capillarity and connate water that appear in reservoir engineering texts, manuals, and papers.

VIII. INTERPRETATIONS OF LEVERETT'S DRAINAGE COLUMN EXPERIMENTS

Once the presence of connate water in zones that produced clean oil was accepted, the problem of determination of connate water distribution in the reservoir by indirect means was addressed. The approach used first by Leverett [16] was to investigate the relationship between capillary pressure and water saturation in various unconsolidated sands.

Today three methods of determining capillary pressure relationships are in common use in the oil industry: (1) pressure membrane apparatus [29], (2) centrifuge [30], and (3) mercury injection [31].

Although these techniques had been applied in other industries, Leverett chose to investigate capillary retention in unconsolidated sands using a drainage column method first reported in the hydrology literature [32] some 40 years earlier. In this method, a long cylinder is packed with sand and allowed to drain under gravity

until flow of water from the column into a free water surface appears to cease. Leverett claimed that this approach was superior to the pressure membrane technique because sample permeability k could be readily measured at the outset of the experiment. However, at that time, the measurement of saturation versus height could only be performed at the end of the experiment by cutting the column into sections and analyzing for water content by drying. This procedure is tedious, and analysis for moisture content involves destruction of the column. Sample permeability, which entered into the $j(s)$ function correlation, could have been measured in a separate experiment or estimated from the Kozeny equation for clean sands. Note that the $j(s)$ function correlation $(\Delta\rho gh/\sigma) \sqrt{(k/\phi)}$ as applied to clean well-sorted sands is very similar to the P_{cR}/σ correlation used by Haines since porosity ϕ is nearly constant for random packings of equal-sized beads, and permeability is proportional to the square of the bead or particle radius R .

The saturation profiles for drainage of clean sands measured by Leverett are shown in Fig. 3. The relationship for drainage from 100% initial water saturation features a saturated zone, transition zone, and, above this, a region where water saturation is essentially independent of height. It is in the interpretation of the nature of the water saturation above the transition zone that a great deal of confusion has arisen. Leverett recognized that this constant saturation arises because of lack of water mobility at low saturations and that it did not correspond to capillary equilibrium. He also recognized that this problem could be avoided by measuring mercury injection capillary pressure curves. (His measurements were made with mercury against air. Although no specific data points were given, this was probably the first mention of mercury injection results in the petroleum literature). Using a combination of the mercury results and estimates by Smith [25] of equilibrium saturations, Leverett provided a capillary pressure curve that was corrected for lack of equilibrium at low saturations (see Fig. 3). Leverett also measured imbibition curves for capillary rise into an initially dry column. He stated: "It appears likely that the conditions under which hydrocarbons accumulate in and are produced from the earth will lead to distributions of fluids corresponding more closely to the imbibition equilibrium than to the drainage equilibrium."

Corrections to the imbibition curve for entrapment of nonwetting phase were also estimated (see Fig. 3). Leverett's results for imbibition into dry sand rather than for a packing having an initial water saturation may not be appropriate. However, the basic question of whether drainage or imbibition curves apply to the virgin reservoir does not appear to have been tackled directly.

Although Leverett's paper is the most widely cited paper on connate water, there has been a general lack of appreciation of several important points.

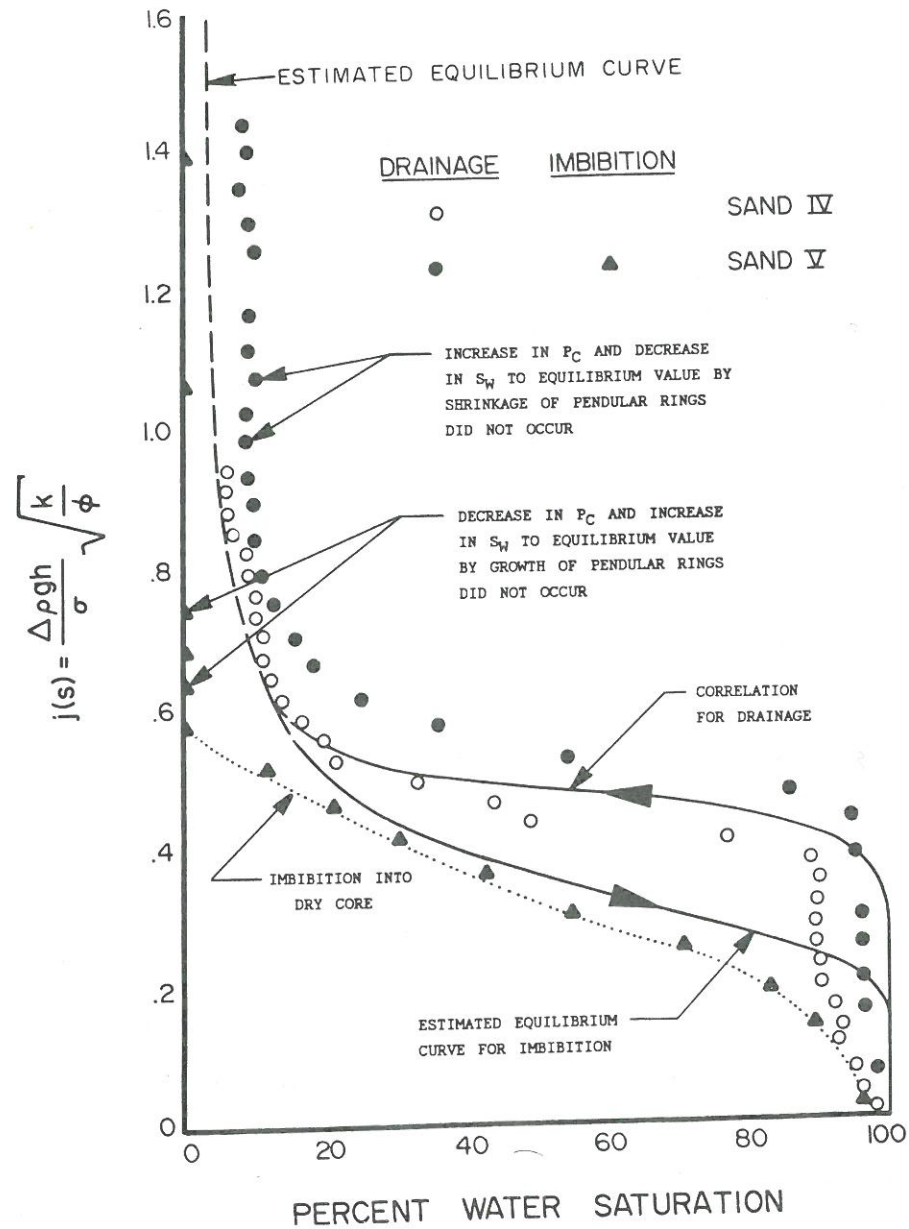


FIG. 3 Capillary pressure data for drainage of clean sands. Dashed line at low saturations is the estimated equilibrium curve. This falls distinctly below the nonequilibrium irreducible saturations of about 10% measured for drainage. The irreducible saturation varies more than is observed for other types of P_c measurement because each point was obtained from drainage column segments. (From Ref. 16.)

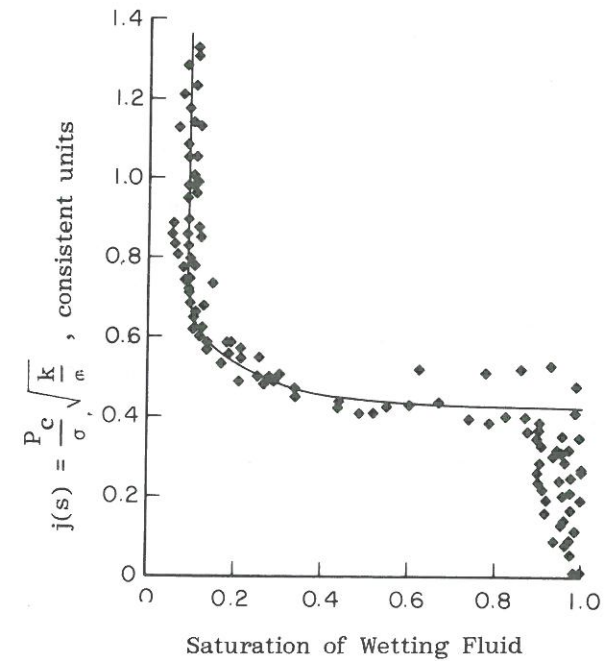


FIG. 4 Leverett's results as presented by Collins [34]. The estimated equilibrium curve (see Fig. 3) has been omitted and an average curve added that passes through the nonequilibrium irreducible saturation data points. Results are nevertheless explained in terms of capillary equilibrium.

1. The experimental curves do not correspond to capillary equilibrium at low saturations.
2. An equilibrium curve was estimated that was considered to be relevant to the equilibrium that can be expected if the reservoir has drained for geologic time.
3. The imbibition curve (corrected for trapping of nonwetting phase—also a nonequilibrium phenomenon) was considered to be applicable to the transition zone.

In the text by Amyx, Bass, and Whiting [33], Leverett's experimental and estimated theoretical curves are shown but their significantly different physical character is not discussed. In the text by Collins [34], *Flow of Fluids Through Porous Media*, Leverett's experimental results are presented but the equilibrium curve is replaced by an average curve for the nonequilibrium experimental data (see Fig. 4). Collins identifies the irreducible saturation directly

with connate water. The explanation is typical of that usually given for the nature of the irreducible saturation.

"All capillary pressure-saturation curves show a characteristically large slope for some low value of wetting fluid saturation. In most cases, the drainage capillary-pressure curve shows that extremely high (approaching infinite) pressures are required to produce an infinitesimal reduction in wetting fluid saturation when a particular limiting saturation is approached. This limiting saturation is called the irreducible saturation (or in the case of water, the connate water saturation). Though the remaining fluid at the irreducible saturation can be removed (by heating for example), for all practical purposes it cannot be removed by injection of non-wetting fluid. Thus, in most physical problems, it will be assumed that P_c becomes infinite at a finite irreducible wetting fluid saturation. For most porous materials a correlation exists between the irreducible wetting phase saturation and permeability. Such a correlation should exist since both quantities are related to 'pore size'."

Strangely, Collins' book also includes a model calculation for capillary equilibrium for a pore formed from four rods, which has the expected general form of an equilibrium curve with results being close to those calculated by Haines for pendular rings in a cubic packing of spheres (see Fig. 2).

The question of whether the drainage or imbibition curve is the more relevant to water distribution in the reservoir is somewhat distinct from the issue of capillary equilibrium. In the present discussion attention will be given mainly to water distribution above the transition zone. We will now consider the form of capillary pressure curves measured on reservoir core samples and the results of water saturations determined by taking core samples using an oil base mud.

IX. COMPARISON OF CONNATE WATER FROM CORES CUT WITH OIL BASE MUDS WITH IRREDUCIBLE WETTING-PHASE SATURATIONS GIVEN BY CAPILLARY PRESSURE MEASUREMENTS

The presence of water in cores cut with oil base muds has been accepted as proof that water coexists with oil in zones that produce water-free oil. Capillary pressure measurements, therefore, seemed to offer a means of determining connate water indirectly from core samples. Following the work of Leverett (1941), several major oil companies published investigations within a short time of each other in which water saturations determined for cores cut with oil base

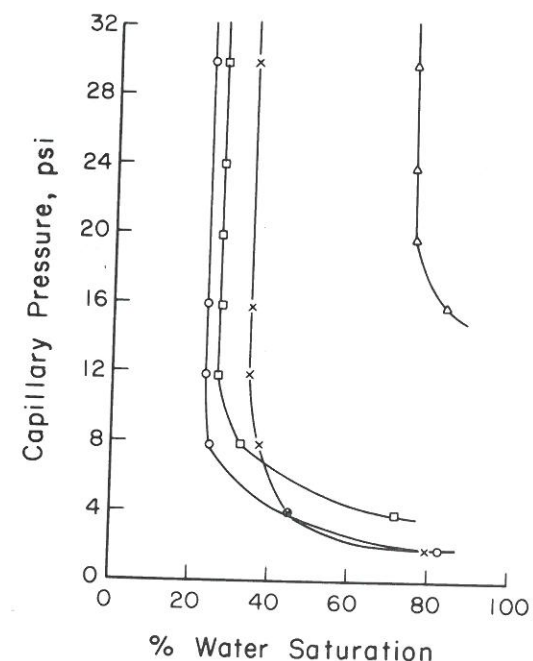


FIG. 5 Examples of restored-state capillary pressure curves frequently described as typical. The well-defined irreducible saturations are the result of nonequilibrium, but this is not usually recognized in analysis and application of results to the reservoir. (After Ref. 36.)

muds were compared with saturations from capillary pressure measurements [29, 35, 36]. Capillary pressure curves, which were described as typical, all featured well-defined irreducible saturations. An example set of data is shown in Fig. 5. In general, the irreducible saturations measured for sandstones were much higher than those measured for beads and sand packs. In discussing these results it was assumed that they represented equilibrium. No attention was given to the distinction made by Leverett and previous investigators between equilibrium and nonequilibrium capillary pressure curves.

The irreducible wetting-phase saturations so obtained were found to be in good agreement with the water saturations measured for the core samples. Results obtained in these three investigations are plotted in Fig. 6. Connate water saturations are seen to range from less than 10% to over 70%. Since the reservoir could be expected to drain to equilibrium over geologic time, this agreement, at first

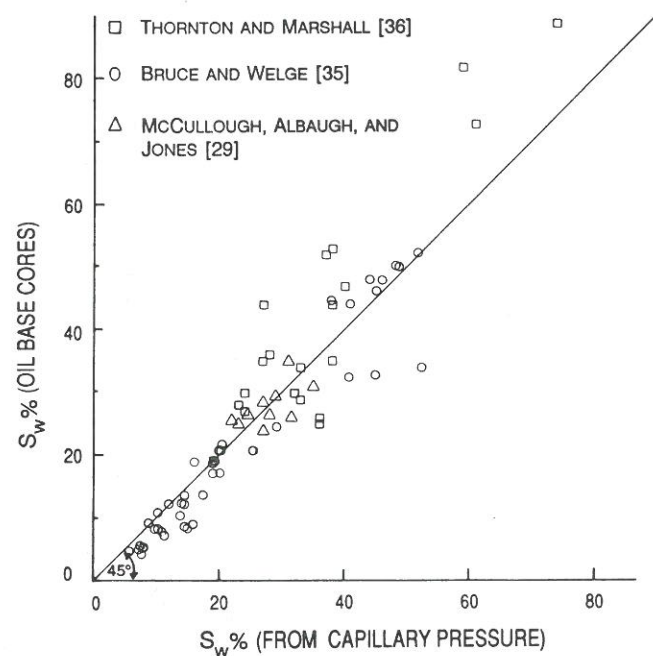


FIG. 6 Plots of water saturation determined for cores taken with oil base muds and water saturations from restored state capillary pressure tests. The agreement implies that the reservoir does not achieve equilibrium even after geologic time, but this was not generally realized. Further comparisons are needed.

sight, appears to support the assumption that the measured curves correspond to capillary equilibrium.

One explanation for the irreducible saturation observed for sandstones commonly given in textbooks and papers (usually where authors make no distinction between equilibrium and nonequilibrium) is that the water is held in microporosity of distinctly smaller pore size than the pores from which water was removed in the course of establishing an irreducible saturation. However, no attempt to check the amount of retained water with the volume of microporosity in the sample has been reported. Furthermore, as will be shown subsequently, this explanation is often inconsistent with the form of capillary pressure curves for mercury injection.

If the irreducible saturation for sandstone samples arises for essentially the same reasons as for beads and clean sands, the agreement between the oil base mud results and the irreducible saturations

implies that the reservoir does not attain equilibrium even after geologic time. If this implication had been appreciated, it seems likely that many more comparisons between oil base mud results and capillary pressure data would have been reported. It also seems likely that much greater attention would have been given to checking whether or not restored-state capillary pressure measurements are valid equilibrium measurements.

X. TWO POSSIBLE CAUSES FOR NONEQUILIBRIUM CAPILLARY PRESSURE CURVES

A strange feature of the three comparative studies mentioned above is that so-called typical capillary pressure curves with well-defined irreducible saturations are, in fact, not typical of the forms of curves measured in other investigations. It was pointed out earlier that mercury injection curves in all likelihood give equilibrium curves. For example, results of mercury injection to over 120 atm reported by Purcell clearly approach the zero wetting-phase saturation asymptotically [31]. This is because escape of the wetting phase at low mobility is not a problem when this phase is essentially a vacuum. In some publications, mercury injection curves of the form that would be expected if equilibrium is attained are in good or at least reasonable agreement with restored-state results, with the latter also not showing well-defined irreducible saturations [31, 37] (see Fig. 7). For convenience in discussion, curves of this type will be called equilibrium capillary pressure curves. (It is recognized that absence of a well-defined irreducible saturation does not necessarily imply that the data corresponds to equilibrium.)

In 1986 Dullien, Lai, and MacDonald [38] reported on the hydraulic continuity at low wetting phase saturations. The criterion for recording a data point was that the rate of saturation change was less than 1% of that observed after increasing the applied capillary pressure. Capillary pressure curves for Berea sandstone of the form expected for equilibrium were obtained with water saturation being reduced to 10% at a capillary pressure of 15 psi (see Fig. 8). In a more recent paper by Dullien et al. [39], saturations achieved by drainage of etched spheres, in contrast to smooth spheres, gave very low saturations at high capillary pressure. However, comparison of the reported saturations for etched beads (Fig. 2 of citation) with the much lower saturations of the equilibrium curves of Fig. 2 (this chapter) demonstrates that they were still distinctly higher than equilibrium values.

In the light of these results and other comparisons between restored state, centrifuge and mercury injection results which do not give a well-defined irreducible saturation, it would appear that results featuring an irreducible saturation do not represent equilibrium.

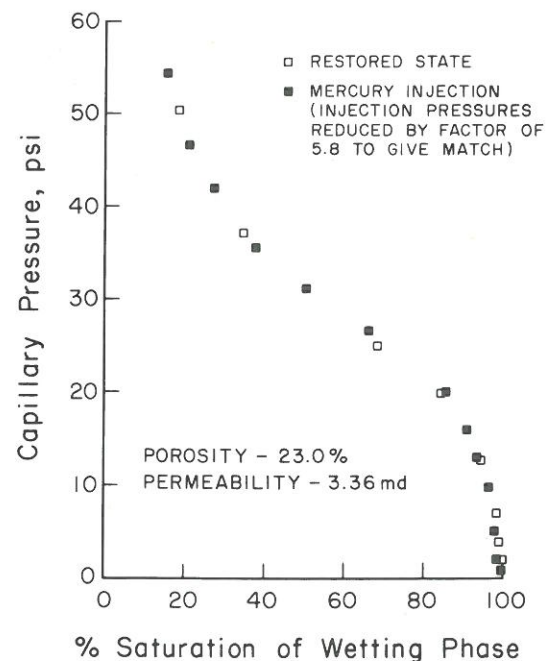


FIG. 7 Capillary pressure curves reported by H. W. Brown [37]. Results for mercury are expected to be at equilibrium because the wetting phase (vacuum) has infinite mobility. The agreement in curve shape obtained for the two techniques implies that the restored state tests also gave equilibrium (in contrast to the type of curve shown in Fig. 5.)

Also, the microporosity explanation of irreducible minimum wetting phase saturations is not applicable.

Two possible forms of nonequilibrium condition may apply to the results for sandstones: (1) During drainage, a fraction of the wetting phase becomes essentially disconnected to give isolated capillary structures somewhat analogous to those found for sphere packings. (A possible explanation of why irreducible saturations are often much higher for sandstones than for beads will be discussed in the following section.) (2) During drainage, hydraulic contact between the membrane and the core is lost so that the irreducible saturation is an artifact of the method. If this is true, the agreement between oil base mud results and the capillary pressure results is extremely surprising. On the other hand, loss of contact with the membrane would be consistent with the observation that

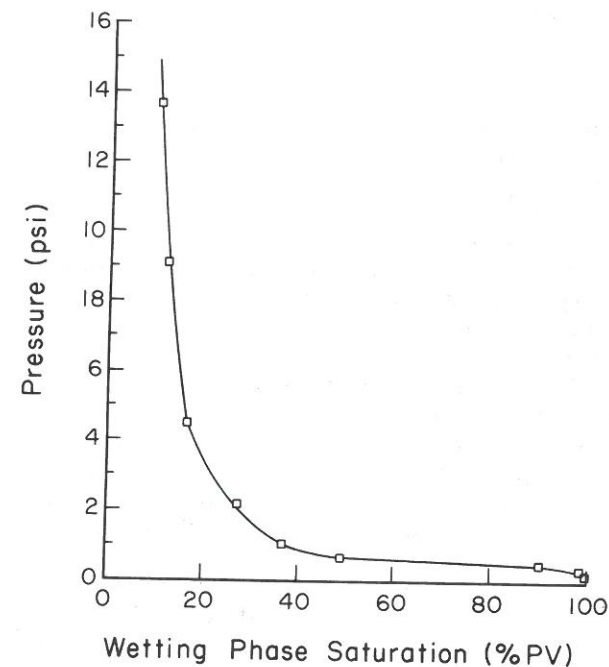


FIG. 8 Capillary pressure data for fired Berea sandstone reported by Dullien et al. [38].

S_{wir} increases with decrease in permeability, assuming that hydraulic continuity at the membrane is lost at about the same pressure for core samples of differing permeability.

XI. MAGNITUDE OF IRREDUCIBLE MINIMUM WETTING-PHASE SATURATIONS

In the following discussion it is accepted that there are circumstances (such as the 7% given by random packings of smooth spheres [40]) where a well-defined irreducible wetting phase saturation S_{wir} is obtained because of the very low mobility of the wetting phase. In early work much attention was given to correlating S_{wir} with permeability [35, 36]. Correlations were obtained but they appeared to be specific to individual formations. Very little effort was put into determining why this variation should be observed. The general trend was for the irreducible saturation to increase as permeability decreased. This may have appeared satisfying intuitively because capillary forces can be expected to increase as pore size decreases.

However, this interpretation is naive because it fails to recognize the mechanisms and scaling laws that govern retention of irreducible saturations. For a random packing of spheres, an irreducible saturation of 7% is retained that is independent of sphere size over a wide range of conditions. Permeability, on the other hand, depends on the square of the sphere size. Thus for this definitive example, the trend of increasing irreducible saturation with decreasing permeability is not observed.

Nevertheless, this intuitive argument has even been extended to sphere packs. Buckles [41] claimed that the irreducible saturation could be changed by varying particle size and area, and that a wide range of irreducible saturations could readily be obtained for a rhombohedral packing of spheres. (Measurements would have disproved this claim.) A close estimate of the irreducible saturation for a hexagonal packing can be made from the drainage pressure, the volume of a drained pendular ring at this pressure, and the coordination number of the packing. Thus the correlations between S_{wir} and petrophysical properties such as permeability and porosity that have been developed for natural sandstones must be viewed as empirical.

It has also been shown that irreducible saturations remain close to 77% for well-mixed aggregates formed from beads of different sizes. However, if a heterogeneous packing is constructed so that pockets of wetting phase in low-permeability zones become isolated before the capillary penetration pressure for that zone is exceeded, very large increases in irreducible saturation can be achieved. Thus it is heterogeneity of pore structure rather than permeability that determines the magnitude of the irreducible saturations. For this reason the irreducible saturation has been proposed as an index of packing heterogeneity [40, 42].

The effect of heterogeneity on retained water saturation was demonstrated by measuring S_{wir} for two unconsolidated core samples as recovered using a rubber sleeve core barrel, and then after mixing and repacking each core. Capillary pressure measurements from core analysis reports showed the samples gave well-defined irreducible saturations of 31.5% and 19% as recovered. After mixing, the S_{wir} decreased from 31.2% to 13.2% in one core and from 19% to 9.8% in the other. The difference was ascribed mainly to the effect of homogenizing the core sample [42].

Dullien et al. [38] observed slow drainage of water that was at first retained in heterogeneities formed from smaller size beads than the matrix. It was concluded that a well-defined irreducible saturation was not attained. This result appears contrary to the behavior described above, but there are several possible reasons for the observed behavior. These include time of observation, ratio of bead sizes (insufficient contrast in capillary drainage pressures), effects of sintering at 720°C on pore size contrast, effects of dyes on wet-

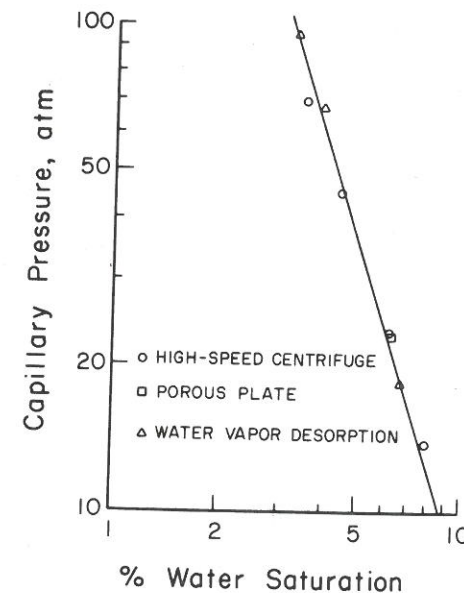


FIG. 9 Relationships between capillary pressure and water saturation for Berea sandstone at high capillary pressures. Results for three distinctly different methods of measurement are in close agreement.

tability, and effect of cleaning procedure (the cleaning solution "Chemsolve" used by Dullien et al. contains potassium hydroxide, which will attack and possibly roughen the glass surface). With respect to the reservoir problem, as with previous investigators who measured equilibrium (mercury injection) data, the results of Dullien et al. point to the unlikelihood that connate water saturation in reservoirs that have drained for geologic time remains at the irreducible saturation measured using a restored-state procedure.

There is now considerable evidence that Berea sandstone, the industry's most commonly used test medium, can be taken down to saturations of about 10% and lower (see Fig. 9) by a variety of desaturation procedures [14, 38, 43, 44]. Such low saturations can probably also be attained for other natural sandstones. Nevertheless, useful operational definitions of irreducible saturations, which provide a unique type of information about pore structure, can still be formulated in terms of the very large decreases in rates of drainage at low water saturations. Thus the definitions would be tied to the severe reduction in mobility of the wetting phase as desaturation progresses.

Much of the discussion of equilibrium at low wetting-phase saturations is qualitative in nature. In general, the ability for equilibration to occur via films retained at drained smooth solid surfaces, even under spreading conditions ($\theta = 0^\circ$), is often overrated. Vapor-phase equilibration is extremely slow at low capillary pressures and would easily be masked by very small temperature gradients in the system. Insufficient attention has been given to the quantitative evaluation of the contributions of bulk water held by microporosity, surface roughness, and pore corners to wetting phase mobility at low water saturations. Questions relating to the stability of wetting films [45, 46] and the effect of wettability on mobility of water also need to be investigated.

XII. WETTABILITY

The effect of wettability on connate water distribution and electrical resistivity is a complex subject and only a few brief points will be made here. Swanson [47] has argued that, even if reservoirs are not generally strongly water wet as was once believed, the connate water distribution in a virgin reservoir corresponds to drainage from 100% water saturation at low contact angle. This provides a rationale for the practice of determining saturation exponents for drainage at what are intended to be strongly water-wet conditions. Interest is growing in measuring electrical properties with oil and water as the fluid phases [48], and until recently [49, 50] little work had been reported for which the oleic phase is crude oil.

In examining the effect of wettability on liquid retention for uniformly wetted systems, Morrow [13] found a fairly small but systematic decrease in retained liquid at a given curvature with increase in contact angle. Low reservoir water saturations are often identified with oil-wet reservoirs. However, some interesting results that appear somewhat to the contrary to this trend have been made for fresh, cleaned, and restored cores. Richardson et al. [51] reported low entry pressures for fresh cores, but a relatively high irreducible water saturation. After cleaning the core, the entry pressures were much higher, but the irreducible saturation was reduced significantly (Fig. 10a). Comparable shifts have been reported by Rühl et al. [52], but with the drainage curve for fresh and restored cores showing similar but unusual shape (Fig. 10b). Recently O'Meara et al. [53] presented centrifuge results for which standard cleaning by Soxhlet extraction with chloroform/methanol solvent gave comparably low entry pressures. Irreducible saturations were not observed, but distinctly higher water saturation at higher capillary pressure was measured for inadequately cleaned cores. A duplicate plug cleaned by flushing with pyridine followed by chloroform/methanol gave drainage curves that matched mercury injection results

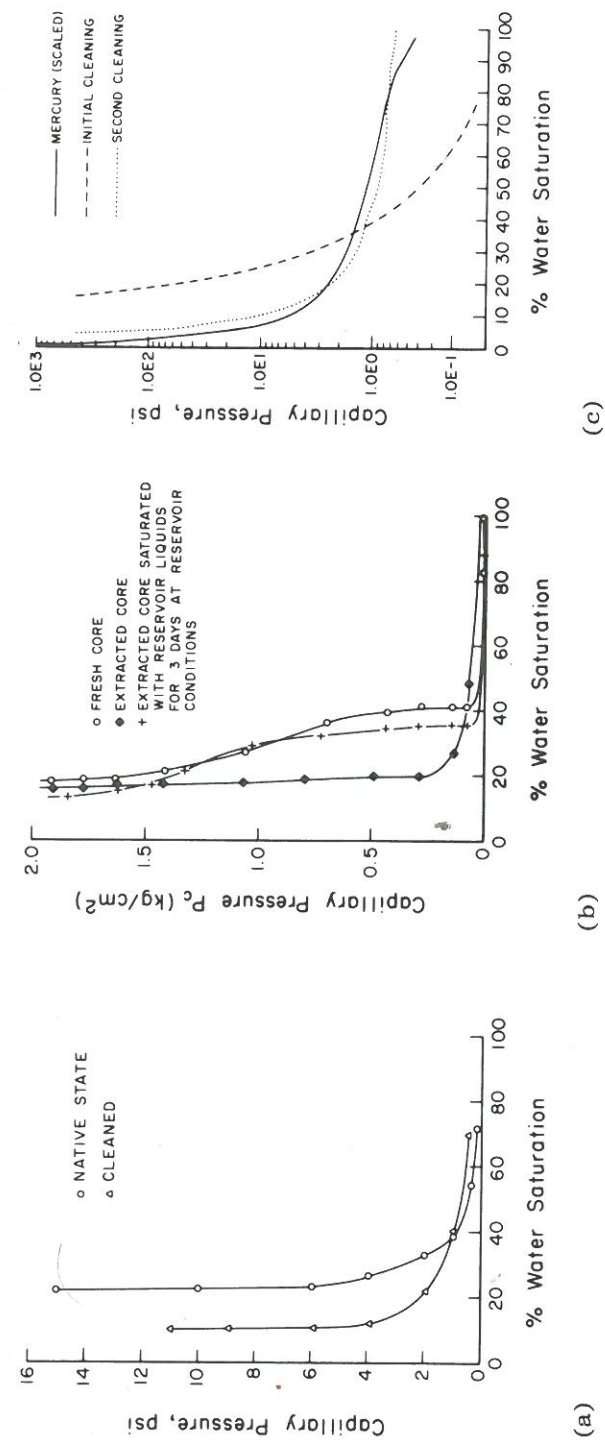


FIG. 10 Effect of wettability on form of capillary pressure curves for reservoir core samples: (a) native state and cleaned cores [51]; (b) fresh, extracted and restored cores [52]; (c) mercury, initial cleaning, second cleaning [53].

(Fig. 10c). Comparisons of drainage capillary pressures for refined oil and crude oil as displacing phases provide further examples of the type of shift in capillary pressure curve described above [49, 50].

It is thus possible that inadequate cleaning procedures have often been a factor in the observation of irreducible saturation for reservoir core samples. In fact, it is now becoming recognized that standard core cleaning procedures are often inadequate. The increased retention of water in fresh and restored cores is probably related in some way to the low drainage pressures. In effect, there is a larger contrast in entry pressures for mixed wettability systems. This may cause larger fractions of water to be retained at very low mobility.

XIII. RECENT DEVELOPMENTS IN THE MEASUREMENT OF EQUILIBRIUM WATER SATURATIONS

In addition to the forgoing discussion of the nature of equilibrium saturations, there have been a number of interesting recent developments. Apart from mercury injection measurements, much of the early work on capillary retention was conducted at pressures of less than about 30 psi. At these pressures, changes in surface curvature produce only very small lowering of vapor pressure. However, a modern high-speed core-analysis centrifuge can produce air/brine capillary pressures of up to about 1000 psi. For water/air, a relative humidity of 95% corresponds to a similar capillary pressure level. Capillary pressure measurements on low-permeability sandstones have been conducted in which centrifuge data was extended to extremely high pressures by measurement of desorption isotherms [15]. Continuous desaturation of the sandstones was obtained with increase in pressure to the stage where essentially all retained water is held by physical adsorption (about 60% relative humidity). Reasonable comparison of these results with high-pressure mercury injection (up to 54,000 psi) was also found [54]. Melrose [55] compared water retention in Berea sandstone for centrifuge, porous plate, and vapor pressure desorption at very high capillary pressures and found excellent agreement (see Fig. 9) between results obtained by the three methods at very low water saturations (<10%). The vapor pressure desorption method has special significance, because the equilibration mechanism will be through the vapor phase and is no longer dependent on the mobility of the bulk water. Vapor pressure desorption measurements provide an especially useful approach to investigation of extremely small pores down to the order of molecular size. Such measurements can also be used to test the notion that observed irreducible saturations represent capillary equilibrium because the retained water is held in microporosity.

With respect to water distribution in the reservoir it would seem highly reasonable to assume that reservoirs can achieve capillary equilibrium by drainage given geologic time. However, as pointed out above, this assumption is inconsistent with the observed agreement between water saturations measured with oil base muds and irreducible saturations measured in capillary pressure tests. Thus, further comparisons are needed between water saturations measured for oil base cores and wetting-phase saturations from capillary pressure measurements at curvatures corresponding to the height at which the core was recovered from the reservoir. If reservoirs are at capillary equilibrium then water saturation must decrease continuously with height above the transition zone. Under these circumstances it becomes appropriate to seek correlations that take this into account. Thus, in contrast to most empirical correlations for connate water, the height at which the core is taken from above the free water surface should also be included in some way since this sets the capillary pressure in an equilibrium system.

XIV. CONCLUSIONS

1. There are serious inconsistencies in the literature on connate water that center around whether or not reservoirs have attained hydrostatic equilibrium above the transition zone (such that $P_c = \Delta\rho gh$) and the circumstances under which capillary pressure data represent equilibrium.
2. Irreducible saturations are usually observed because of the extremely low mobility of the wetting phase. Generally they are symptomatic of nonequilibrium. Irreducible saturations are sometimes ascribed to microporosity, but this explanation has not been checked quantitatively.
3. If reservoirs are at equilibrium, the concept of an irreducible saturation above the transition zone, as commonly described in reservoir engineering manuals and textbooks, is probably invalid, even allowing for differences in lithology.
4. If reservoirs do achieve capillary equilibrium, estimates of oil and gas in place will be much higher than predicted using capillary pressure results that feature irreducible saturations.
5. If reservoirs are at capillary equilibrium, the observation that is most difficult to explain is the agreement that has been reported between irreducible saturations and water saturations measured with oil base muds. A disconcerting aspect of the claims with respect to this agreement is that capillary pressure curves that exhibit a well-defined irreducible saturation are described as typical and no recognition is given to the interpretation of the irreducible saturation as a nonequilibrium condition.

6. If reservoirs are at capillary equilibrium (capillary pressure proportional to height above the free water surface), then the level of the capillary pressure should enter into correlations of connate water with core properties.
7. Mercury injection provides the most reliable approach to obtaining equilibrium capillary pressure data for drainage over a wide saturation range. This is because the wetting phase, a vacuum, always has infinite mobility. However, effects of wettability at low wetting-phase saturations need to be better characterized and a correction for the contribution of wetting films to the saturation needs to be applied.
8. Mercury injection data provide a useful guide to the validity of attempts to obtain equilibrium data by the restored-state technique. Capillary pressure data measured with water as the wetting phase are probably somewhat more representative of the reservoir (notwithstanding reservoir conditions testing) with respect to rock-fluid interactions than the mercury-vacuum system. Agreement in shape of capillary pressure curves measured by restored-state and mercury injection implies that equilibrium data can be obtained by the restored-state technique.
9. The most striking inconsistency in the literature is the fact that pressure membrane data for cores taken with oil base muds feature well-defined irreducible saturations, whereas in other investigations involving comparisons with mercury injection data, the pressure membrane data match reasonably well with the equilibrium form of the mercury data.

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REFERENCES

1. P. D. Torrey, Producers Monthly 30(5):8-11 (1966).
2. R. J. Schilthuis, Trans. AIME 127:199-212 (1938).
3. A. D. Garrison, A. P. I. Drilling and Production Practice 130-135 (1935).
4. N. R. Morrow, J. Can. Pet. Technol. 10:38-46 (1971).
5. N. R. Morrow, J. Can. Pet. Technol. 10:47-55 (1971).
6. J. C. Melrose, in Symposium on Wetting, S.C.I. Monograph, No. 25, London, 1967, pp. 123-143.
7. J. C. Melrose, Can. J. Chem. Eng. 48:638-644 (1970).
8. J. C. Melrose, Langmuir 3:661-667 (1987).
9. J. C. Melrose and C. F. Brandner, J. Can. Pet. Technol. 13:54-62 (1974).
10. N. R. Morrow, Ind. Eng. Chem. 62(6):32-56 (1970).
11. D. C. Dyson, in Progress in Surface and Membrane Science (J. F. Danielli, ed.), vol. 12, Academic Press, New York, 1978, p. 479.
12. W. B. Haines, J. Agric. Sci. 20:97-116 (1930).
13. N. R. Morrow, J. Can. Pet. Technol. 15:49-69 (1976).
14. J. C. Melrose, SPE Reservoir Eng. 3:913-918 (1988).
15. J. S. Ward and N. R. Morrow, SPE Formation Evaluation 2:345-355 (1987).
16. M. C. Leverett, Trans. AIME 142:152-168 (1941).
17. G. L. Hassler, E. Brunner, and T. J. Deahl, Trans. AIME 160:155-174 (1945).
18. M. Muskat, Trans. AIME 179:119-127 (1948).
19. B. F. Swanson, Log Analyst 26(6):42-52 (1985).
20. M. McKellar and N. C. Wardlaw, AAPG Bull. 72(6):765-771 (1988).
21. R. A. Fisher, J. Agric. Sci. 16:492-505 (1926).
22. J. C. Melrose, AIChE J. 12:986-994 (1966).
23. J. C. Melrose and G. C. Wallick, J. Phys. Chem. 71:3676-3678 (1967).
24. W. O. Smith, Physics 4:184-193 (1933).
25. W. O. Smith, Physics 4:425-438 (1933).
26. W. O. Smith, Paul D. Foote, and P. F. Busang, Physics 1:18-26 (1933).
27. B. A. Keen, The Physical Properties of the Soil, Longmans Green, London, 1931.
28. J. M. Dallavalle, Micromeritics—The Technology of Fine Particles, 2nd ed., Pitman, New York, 1948.
29. J. J. McCullough, F. W. Albaugh, and P. H. Jones, A.P.I. Drilling and Production Practice 180-187 (1944).
30. G. L. Hassler and E. Brunner, Trans. AIME 160:114-123 (1945).
31. W. R. Purcell, Trans. AIME 186:39-46 (1949).
32. F. H. King, Principles and Conditions of the Movements of Ground Water, U.S. Geological Survey, 19th Annual Report, Part II, 1897-1898, p. 59.
33. J. W. Amyx, D. M. Bass, Jr., and R. L. Whiting, Petroleum Reservoir Engineering, McGraw-Hill, New York, 1960.
34. R. E. Collins, Flow of Fluids through Porous Materials, Petroleum Publishing Co., Tulsa, Okla., 1976.
35. W. A. Bruce and H. J. Welge, Oil Gas J. 46(12):223 (1947).
36. O. F. Thornton and D. L. Marshall, Trans. AIME 170:69-77 (1947).
37. H. W. Brown, Pet. Trans. AIME 192:67-74 (1951).
38. F. A. L. Dullien, F. S. Y. Lai, and I. F. MacDonald, J. Colloid Interface Sci. 109:201-218 (1986).
39. F. A. L. Dullien, C. Zarcone, I. F. MacDonald, A. Collins, and D. E. Bochar, J. Colloid Interface Sci. 127(2):362-372 (1989).

40. N. R. Morrow, Chem. Eng. Sci. 25:1799-1815 (1971).
41. R. S. Buckles, J. Can. Pet.:42-52 (Jan-Mar. 1965).
42. N. R. Morrow, A.A.P.G. Bull. 55:514-522 (1971).
43. R. E. Bretz, S. L. Welch, N. R. Morrow, and F. M. Orr, Jr., Mixing During Two-Phase Steady-State Laboratory Displacements in Sandstone Cores, paper SPE 15389 presented at the 61st SPE Annu. Tech. Conf. and Exhibition, New Orleans, La., Oct. 5-8, 1986.
44. J. C. Melrose, in Proceedings, IUPAC Symposium on the Characterization of Porous Solids, Elsevier, Amsterdam, 1988, pp. 253-261.
45. J. S. Buckley, K. Takamura, and N. R. Morrow, SPE Formation Evolution (Aug. 1989) 332-340.
46. J. C. Melrose, Interpretation of Mixed Wettability States in Reservoir Rocks, paper SPE 10971 presented at the 57th Annual Fall Technical Conf. and Exhibition, New Orleans, La., Sept. 26-29, 1982.
47. B. F. Swanson, J. Pet. Technol. (August) 1459-1464 (1980).
48. D. G. Longeron, M. J. Arguad, and J. P. Feraud, Effects of Overburden Pressure, Nature, and Microscopic Distribution of the Fluids on Electrical Properties of Rock Samples, SPE 15383 paper presented at 61st SPE Annu. Tech. Conf. and Exhibition, New Orleans, La., Oct. 5-8, 1986.
49. D. G. Longeron, M. J. Arguad, and L. Bouvier, Resistivity Index and Capillary Pressure Measurements Under Reservoir Conditions Using Crude Oil, SPE 19589 paper presented at the 64th SPE Annu. Tech. Conf. and Exhibition, San Antonio, Tex., Oct. 8-11, 1989.
50. E. Soendena, F. Bratteli, K. Kolltveit, and H. P. Normann, A Comparison between Capillary Pressure Data and Saturation Exponent Obtained at Ambient Conditions and at Reservoir Conditions, SPE 19592 presented at the 64th SPE Annu. Tech. Conf. and Exhibition, San Antonio, Tex., Oct. 8-11, 1989.
51. J. G. Richardson, F. M. Perkins, Jr., and J. A. Osoba, J. Pet. Technol. (June):86-91 (1955).
52. W. Rühl, C. Schmid, and W. Wissmann, Erdöl und Kohle-Erdgas-Petrochemie 16(6-I):504-511 (1963). English translation available from the John Crerar Library, Trans. No. 82-21848.
53. D. J. O'Meara, Jr., G. J. Hirasaki, and J. A. Rohan, Centrifuge Measurements of Capillary Pressure: Part 1—Outflow Boundary Condition, SPE 18296 presented at 63rd SPE Annu. Tech. Conf. and Exhibition, Houston, Tex., Oct. 2-5, 1988.
54. N. R. Morrow, J. S. Buckley, M. E. Cather, and K. R. Brower, Rock Matrix and Fracture Analysis of Flow in Western Tight Gas Sands—Final Report, Feb. 1990 U.S. D.O.E. In press.

55. J. C. Melrose, Valid Capillary Pressure Data at Low-Wetting Phase Saturations, paper SPE 18331 presented at the 63rd Annu. Fall Tech. Conf. and Exhibition, Houston, Tex., Oct. 2-5, 1988.