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Discussion of Valid Capillary Pressure Data at Low Wetting-Phase Saturation

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Melrose (Feb. 1990 *SPERE*, Pages 95-99) presented the results of water/air displacements on several Berea sandstones at low wetting-phase saturation using a very-high-speed centrifuge and a semipermeable membrane with a high working differential pressure. In these experiments, air invaded all the pores of the samples after the applied pressure exceeded a certain value (say at most 1 bar).

My concern is the use of the term "capillary pressure" for the differential pressure larger than the value at which all the pores are invaded physically. The following discussion provides a basis for saying that the reduction of wetting-phase saturation at a differential pressure higher than that at the start of the sharp P_c increase is not a capillary pressure process; a shearing or tangential force causes the reduction of the irreducible liquid saturation thickness.

If the laboratory-measured differential pressures at low wetting-phase saturation are used as the prevailing capillary pressures between two phases in any reservoir, while the irreducible wetting phase is assumed to be under hydrostatic conditions, one can calculate a negative wetting-phase pressure when the reservoir pressure drops below a certain positive value. This could cause a problem when high-relief reservoirs are studied with a commercial simulator.

Capillary pressure [$P_c=\sigma(1/r_1+1/r_2)$, where r_1 and r_2= principal radii, and σ=interfacial tension] represents the required pressure difference to transform the initial contact into a moving interface during flow through a conduit initially saturated by a pure component. I say a pure component because the solid surface may preferentially adsorb more of the more-wetting component than is present in a miscible mixture.

In a capillary tube, the wetting phase reaches the "irreducible" saturation (adsorbed film) when $\Delta p=P_c=2\sigma/r$ ($\theta=0$) is exerted on the wetting phase by the nonwetting phase at the entry of the tube. Kussakov and Mekenitskaya[1] measured a water-film thickness of about 0.1 μm in a capillary tube initially filled with water and displaced by air or hydrocarbons. When a capillary tube is invaded, it may seem that $\Delta p=\sigma/r$ between the water film surrounding the nonwetting phase; the P_c restriction for the nonwetting phase to flow through the tube is zero. If a pressure gradient larger than the displacing pressure between the two ends of the capillary tube is applied, the irreducible water film decreases further. In this case, the pressure difference between the water film and each point in the capillary tube will be slightly less than σ/r because r is now $r+\epsilon$, though the pressure within the capillary tube, p, is much higher than $2\sigma/r$. Therefore, the P_c relationship does not apply to a capillary tube at or beyond the irreducible saturation.

Similarly, the capillary pressure of a saturated porous sample represents the entry pressure of different pores by the nonwetting phase.[2] After a porous sample is displaced to its "irreducible" saturation, the nonwetting phase flows through the sample without P_c restriction. This implies that the irreducible saturation is part of the rock as far as P_c is concerned.

Several studies were made on different water-wet sandstone outcrops to show how the wetting saturation changes with increasing nonwetting-phase pressure. A highly accurate porous-plate apparatus developed by the Inst. Français du Pétrole* was used. In the experiments, three different fluid pairs were used in a Vouge core sample. Afterward, the core sample was divided into two parts and the P_c of both pieces was measured by mercury injection. Results of the four experiments, shown in **Fig. D-1**, indicated the following.

1. The P_c/saturation relationship is proportional to the σ of each fluid pair up to a pressure before the start of the sharp nonwetting-phase pressure increase, with a slight deviation toward the lower wetting saturation.
2. The common laboratory and field observations of a higher water/oil than water/N_2 "irreducible" saturation (σ=36 dynes/cm compared with σ=71 dynes/cm), clearly demonstrates that the vertical part of these measurements does not obey the defined P_c relationship.
3. The water/oil experiment, with a σ about one-half that of water/N_2 and an irreducible saturation about twice that of water/N_2, indicates the invasion of nearly all the accessible pores. Therefore, the transition from the P_c-related (flat portion) and the vertical portion that does not obey the P_c relationship mainly represents further wetting-phase desaturation of the already invaded pores with smaller throats by the nonwetting phase (end effect at different pore levels).

Therefore, it is evident that an essential difference exists between the minimum differential pressure leaving a residual saturation and the pressure difference across the interface of the residual saturation at either the same pressure or a higher differential pressure at which the residual saturation is further reduced. The microscopic process of the last case is further discussed below.

Deryagin[3] noted the presence of a relatively immobile water film of 0.15 μm, or 0.075 μm on each surface, between two horizontal glass lenses under stationary conditions. Bascom *et al.*[4] studied both upward and downward movements of squalane ($C_{30}H_{50}$) on polished vertical steel. They measured a fairly uniform film thickness of more than 0.2 μm during upward movement. Deryagin and Kussakov[5] measured different film thicknesses up to 2 μm on mica. These experiments seem to suggest that the adsorbed layer (irreducible saturation) has negative pressure that increases in magnitude with height. This obviously could not be the case because negative liquid pressure with no curvature in the case of a flat plate and a constant $\Delta p=\sigma/r$ in a capillary tube has no meaning. This behavior is similar to that of porous media after irreducible saturation is established.

As the pores are invaded, the P_c between two moving phases is smaller in each pore body than the pore's throat entry pressure because the mean curvature between two phases in each pore is flatter than that of the throat. The experiments of Yuan and Swanson[6] confirm these statements. A fully invaded pore contains pendular rings with adsorbed film covering the remaining surface of the grains. As in the capillary tube, it would be hard to conceive that after the P_c in a pore decreased, it would jump to a higher value corresponding to the apparent average pendular curvatures in that pore. Except for the permeability reduction, a fully invaded sample allows the nonwetting phase to flow in a manner similar to the wetting phase—i.e., without P_c restriction. The reported gas/oil gravity drainage experiments[7] with the presence of irreducible water saturation in sand-packed columns show that oil saturation approaches zero, indicating the absence of P_c trapping between water and oil. Therefore, the presence of pendular rings with possible small curvatures does not constitute a P_c restriction for the nonwetting phase, though microscopically there could be a pressure difference across the stationary interface.

In practice,[8,9] the reduction of the irreducible saturation is associated with exponentially increasing the nonwetting phase pressure. Microscopically speaking, for the term P_c to be used for the process of reducing the irreducible saturation in each pore, it also should correspond to an exponential reduction in the radius of curvature between the two phases. Assuming that the pendular rings contain the major part of the irreducible saturation, when the nonwetting phase pressure is increased from a value of about irreducible to a pressure, say, three times greater, the effective radius of curvature decreases by about the same factor, as shown in **Fig. D-2.** Such reduction of the radius of curvature should correspond to a saturation decrease by the above-mentioned ratio to the power of about 1.7 ($3^{1.7}=5$ times) when $\alpha<20°$ (see Ref. 10) if it fol-

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*Experiments performed by D. Longeron of Inst. Français du Pétrole within the RTEP program, 1988 to Jan. 1991.

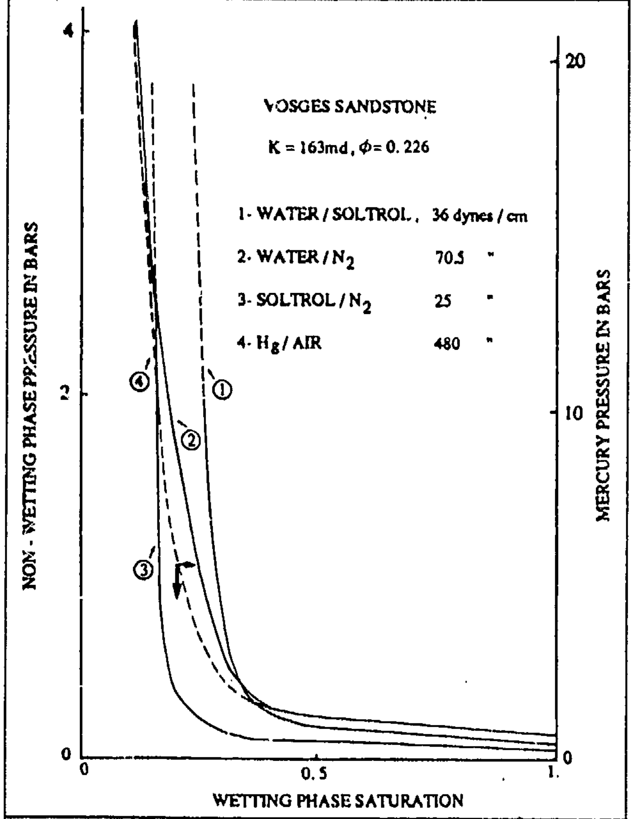

Fig. D-1—Measured porous-plate and mercury-injection capillary pressures for different wetting- and nonwetting-phase fluids (RTEP project).

lows the P_c relationship, whereas it actually decreases by the square root of the saturation, as seen in **Fig. D-3.** That is, the small change in saturation owing to the large pressure change represents a very small difference in the curvature, and therefore the change in the curvature does not follow the P_c relationship.

Deryagin[11,12] derived the following relationship for the film thickness, h, on the solid rod as it is pulled out at a very low velocity, v, from a bulk liquid with a density $\Delta\rho$, viscosity μ, and a surface tension between the two phases σ:

$$h=0.93(\mu v)^{2/3}/(\Delta\rho g)^{1/2}\sigma^{1/6}.$$

The parameters used in the experiments shown in Fig. D-1 are $\Delta\rho(w,N)=1.0$, $\Delta\rho(w,o)=0.25$ g/cm^3, $\sigma_{wN}=70.5$ dynes/cm, $\sigma_{wo}=36$ dynes/cm, $\sigma_{oN}=25$ dynes/cm, and $\mu_o=1.53$ cp. The theoretical water/N_2 to water/Soltrol™ film thickness ratio is 2.27, which is very close to the measured irreducible saturation ratio of 25/11.2=2.32. The theoretical ratio of Soltrol/N_2 to water/N_2 gives 1.82, compared with the measured value of 16.3/11.2=1.46. The smaller Soltrol/N_2 average film thickness is mainly a result of the sample wettability, which is not oil-wet. The reported measured irreducible saturation[13] of 8.3% when air displaces water with $\sigma=71.2$ dynes/cm and $\mu_w=1$ cp and of 8% when air displaces methanol with $\sigma=22$ dynes/cm, $\Delta\rho=0.792$ g/cm^3 and $\mu_m=0.64$ cp gives the theoretical ratio of 0.986, which is also close to the measured ratio of 1.038. Deryagin's equation suggests that after the film-ring saturations are established, the adsorbed film thickness is a function of the wetting-phase viscosity. The Bascom *et al.*[4] experiments show that the longer molecules develop a thicker film on the flat vertical walls, which is also in line with the measured water-film thickness.[1,3]

To further demonstrate that the low wetting-phase saturation (below irreducible) is proportional to the adsorbed film thickness, Deryagin's equation and the measured saturation vs. pressure reported by Melrose (his Fig. 5) are used and the results shown in Fig. D-3. In this calculation, the measured saturation (11.6%) at 6 bar was used as a reference point and g was assumed to be proportional to the applied pressure. The nearly identical calculated and measued values show the applicability of the concept discussed above. That is, the volume of the wetting phase held in a pendular form is related to the adsorbed film thickness approximately by a simple relationship $h=f(S)=a\Delta P^{-1/2}$ when other parameters are constant.

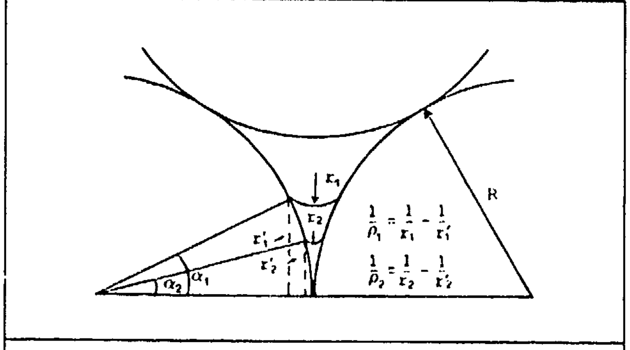

Fig. D-2—Schematic cross section of a pore showing the ratio of effective radii to the radii of the areas below the menisci.

The pendular rings, which probably contain the major part of the irreducible saturation, in an idealized form are the volume under nodoid or hyperboloid surface around the lines connecting the center of two contacting spheres (grains) surrounded by the continuous nonwetting phase. If the pendular rings are assumed to be isolated (i.e., they are not in pressure equilibrium with the adsorbed film in a porous column), an increase in the nonwetting phase pressure would not alter the shape of the rings. This is contrary to the measurements made at high nonwetting phase pressure. Therefore, the pendular rings are in pressure equilibrium through a disjoining pressure with the adsorbed film, as proposed by Deryagin[12]; i.e., the adsorbed film is pulling the pendular ring from all sides.

The force per unit contact area with which the thinner film pulls the thicker pendular ring, the disjoining pressure,[12] is given by $\Pi h=\Delta p$, where h is the film thickness at elevation H from the bulk liquid, Π=disjoining pressure, and Δp=pressure drop across the boundary. This concept also also suggests that the wetting phase exerts a pressure on the solid that is a function of h. At irreducible saturation, the thin film pulls the surrounding pendular rings, developing disjoining pressures that exert an equivalent pressure on the solid grains. This is analogous to an elastic membrane covering a solid sphere. As the elastic membrane is pulled from a point, its thickness is reduced, it exerts normal pressure on the solid, and the resulting frictional forces counterbalance the membrane's weight (it behaves as if the membrane is part of the solid).

The number of water molecules,[1,3] for example, within a diameter of about 2.5×10^{-8} cm extending out of a water-wet solid is about $10^{-5}/2.5\times10^{-8}=400$. As the nonwetting phase pressure is increased to a value of about or below the irreducible saturation, the outer molecules more loosely adhered to the solid grains are removed. This causes the readjustment of all film-ring thicknesses in the porous column, developing a larger disjoining pressure and thus exerting a higher pressure on the solid surface. Therefore, the wetting molecules below the irreducible saturation in a vertical plate, capillary tube, or porous medium are not under hydrostatic conditions. They are lined up horizontally owing to the different forces, and their weight is not added in the vertical direction. In a sense they are like a facade that is attached to the solid wall. To separate each molecular layer from the wall requires an exponentially higher shearing pressure differential across the adsorbed layers.

An important issue in this process is therefore the contact points between the porous plate and a draining porous sample. The experiments of Firoozabadi and Hauge[14] clearly show that two porous bodies with closer grain sizes develop better continuity than two with grain sizes that are farther apart. Review of a large number of sandstone and limestone cores of known specific surface area with large permeability and porosity variations gives an average film thickness of about 2×10^{-5} cm at their irreducible saturations. An example is given by Saidi.[2]

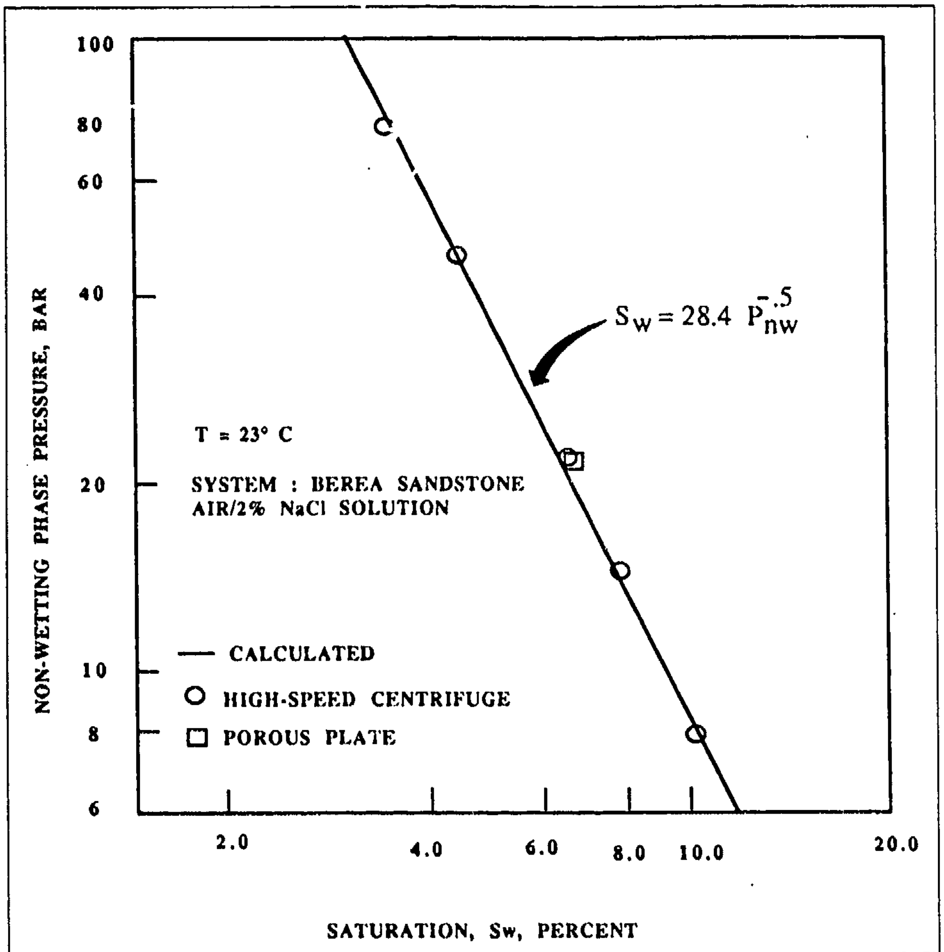

Fig. D-3—Calculated and measured endface saturation vs. endface nonwetting-phase pressure (Data from Melrose's Fig. 5).

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SI Metric Conversion Factors

bar × 1.0* E+05 = Pa
cp × 1.0* E−03 = Pa·s
dynes/cm × 1.0* E+00 = mN/m
in. × 2.54* E+00 = cm
md × 9.869 233 E−04 = μm^2

*Conversion factor is exact.

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