Capillary Pressure and Wettability Measurements Using Micropore Membrane Technique

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Capillary Pressure and Wettability Measurements Using Micropore Membrane Technique

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Introduction

This paper presents improvements in measuring complete capillary pressure (P_c) curves for different wettabilities. The diaphragm method is very accurate and reliable and so far the only method that may give the full loop of P_c curves, forced and spontaneous drainage and imbibition, but has been extremely time consuming. However, recent work (Hammervold and Skjæveland, 1992; Guo and Hammervold, 1993) has shown a significant reduction in experimental time if thin micropore membranes are used instead of porous disks for drainage P_c measurements. Now, this method is extended to the full cycle of P_c curves.

A new coreholder cell, together with two thin membranes and specific procedures, has been developed and tested on sandstone and carbonate cores. Full cycles of P_c curves were obtained and, in addition, the concept of wettability has been quantified by a new index that takes into account the areas between the P_c curves and the saturation axis.

Equipment

A coreholder has been constructed consisting of three parts: two endpieces that can be dismounted separately and a cylinder, which contains the coated core. The diameter of the core is 5 cm and the thickness 2 cm. Fig. 1 shows the coreholder and endpiece, and a cross-section of the arrangement of the endpiece with membrane.

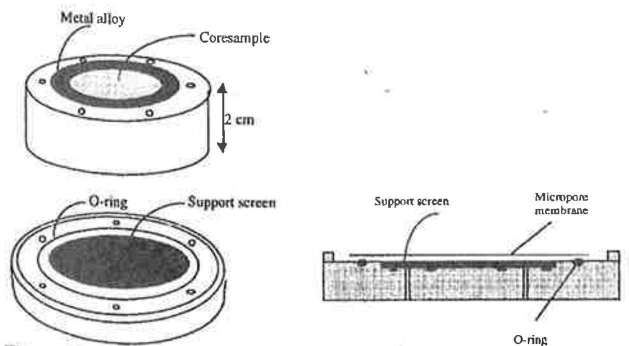

Figure 1: The coreholder and endpiece (left) and a cross-section of the endpiece with membrane.

The cycles of P_c curves were obtained by using thin water-wet and oil-wet membranes. Fluids were brine, refined oil and crude oil. The membranes could be replaced during the experiment. The displaced fluid was produced at atmospheric pressure and the amount recorded by an optical device connected to a micropump which again was connected to a plotter. The differential pressure was applied either by a pressure cell containing oil and nitrogen or by an oil column (for the pressures below 200 mbar) with good accuracy for the differential pressure at low values. When measuring spontaneous imbibition of water, the oil pressure is decreased, and a burette is placed at the outlet to measure the amount of water imbibed. For the forced imbibition curve, the brine pressure is applied in the same manner as for oil pressure during drainage: first by the water column head, and then by a pressure cell containing water and nitrogen.

Experiments

Two types of cores have been used, Vosges Sandstone and Estaillade Carbonate (both outcrops). One core of each material was aged in crude oil and another was measured at native water-wet conditions. P_c cycles consisting of four curves, subsequent to the primary drainage, were measured on four different cores. An Amott-IFP (Cuiec, 1991) test was performed on similar core plugs, both for untreated and aged cores, to check the effectiveness of the aging procedure (Table 2). Drainage curves for water-wet cores were measured by the membrane technique, the standard porous plate technique and by mercury injection for comparison. Core data are in Table 1.

Table 1: Core data

Test No.	1	2	3	4
Core Material	ss*	ss	c**	c
ϕ (%)	21.2	22.0	28.0	27.5
k_g (md)	242	251	106	113
k_w (md)	136	139	54	57
PV (cm^3)	8.10	8.6	10.9	10.8
Treatment	native	aged	native	aged

ss* = sandstone, c** = carbonate

Table 2: Wettability indices.

Core	Amott,	Modified USBM	HL-Index,	Amott-IFP
ss	0.50-0.00 = 0.50	1.47	0.85-0.00 = 0.85	0.78
ss aged	0.12-0.05 = 0.07	0.03	0.77-0.06 = 0.71	0.50
c	0.91-0.01 = 0.90	1.95	0.99-0.02 = 0.97	0.97
c aged	0.02-0.01 = 0.01	0.33	0.01-0.02 = -	-0.44

Attempt to Assign a New Wettability Index: the Hl-index

Data from the spontaneous imbibition and drainage processes are not included in the calculation of the USBM (Donaldson *et al.*, 1969) index. It seems intuitively reasonable that these processes also would characterize the wettability of the system and should be included in an overall wettability index for the sample. Consequently, a new wettability index is suggested, the Hammervold-Longeron index I_{HL}:

$$I_{HL} = I_w - I_o \qquad 1$$

where

$$I_w = B_1/(B_1 + A_2) \qquad 2$$

and

$$I_o = B_2/(B_2 + A_1) \qquad 3$$

where B_1 is the area under the spontaneous imbibition curve, A_2 is the area under the forced imbibition curve, B_2 the area under the spontaneous drainage curve, and A_1 the area under the secondary drainage curve (Fig. 2). The absolute values of the areas are used. The new index may be able to distinguish between mixed- and spotted-wet samples, since a spotted-wet sample would spontaneously imbibe more of the continuous wetting phase than the discontinuous (spotted) phase, and a mixed-wet sample would spontaneously imbibe both fluids. In contrast, an intermediate (homogeneous) core would not imbibe in any direction.

Results

Figs. 3 and 4 show a comparison between drainage P_c curves obtained by the membrane technique and by mercury injection for water-wet carbonate and sandstone cores. There is good agreement between the two measurement techniques, as expected. Mercury injection is believed to be a representative method for measurement of the first part of the drainage curve for water-wet samples (Omoregie, 1986). Fig. 4 also shows a comparison between drainage P_c curves obtained by the membrane technique and by the traditional porous plate method using a sintered alumina plate.

Four complete P_c loops have been measured by the membrane technique on two Vosges Sandstone cores (Figs. 5 and 6), and two Estaillade Carbonate cores (Figs. 7 and 8) for each rock type on both a water-wet core and one aged in crude oil. (The drainage curve for experiment No.2, Fig.6, is not reported.)

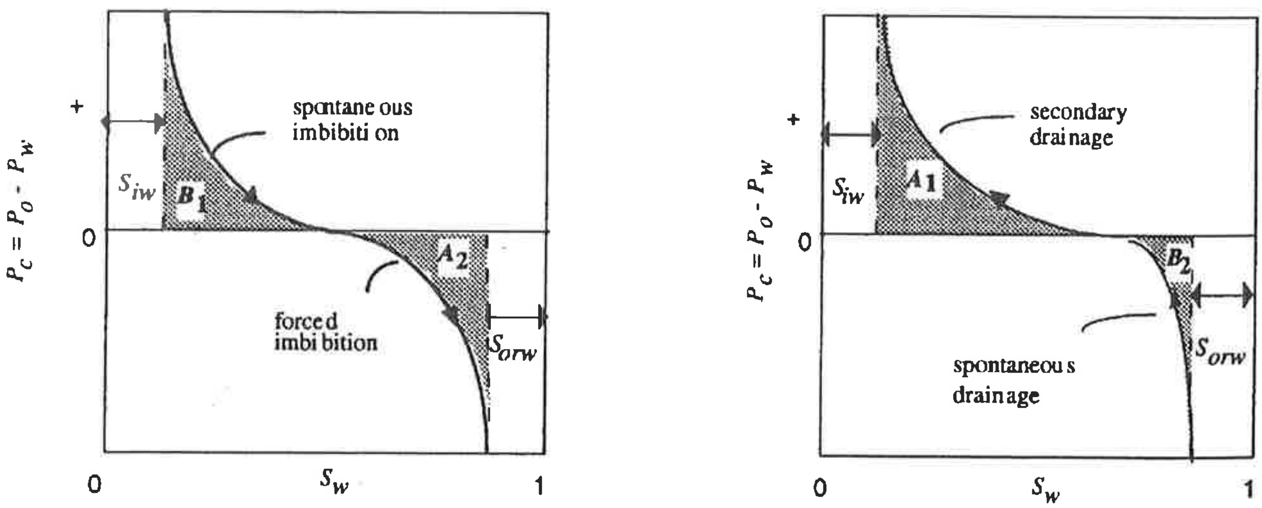

Figure 2: Illustration of areas used for the HL-index determination.

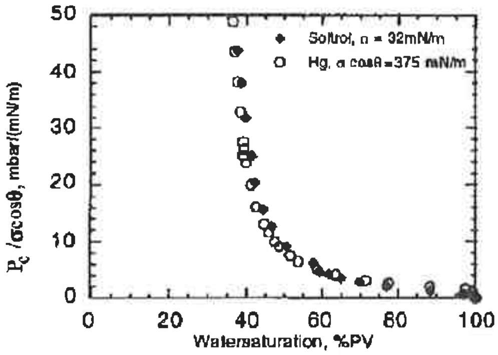

Figure 3: Drainage P_c curves by membrane and mercury injection technique, carbonate.

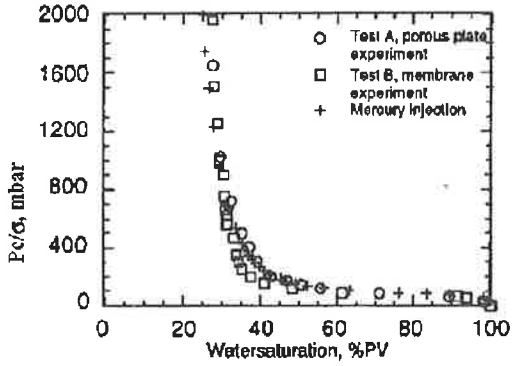

Figure 4: Drainage P_c curves by membrane, porous plate, (disk of sintered alumina) and mercury injection technique, sandstone.

The HL-index was calculated for the four cores. Also the Amott (Amott, 1959) and the USBM-index can be calculated from the data, although the method originally described for these tests is not used. For the calculation of the Amott index, the saturation intervals are taken from the membrane measurements. For the calculation of the USBM-index, the areas under the secondary drainage and forced imbibition curves from the membrane measurement (denoted by A_1 and A_2 in Fig. 2) are used. The wettability indices are listed in Table 2.

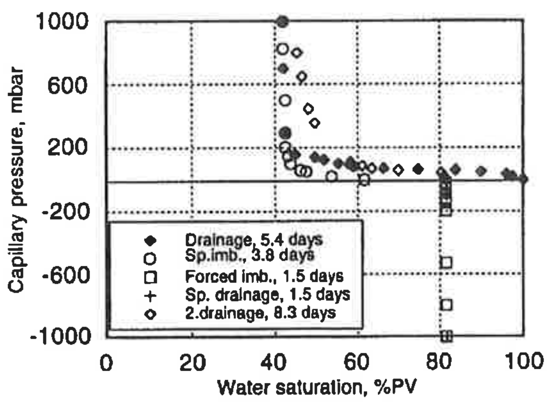

Figure 5: P_c loop (test #1), Vosges Sandstone, water-wet, I_{HL} = 0.85.

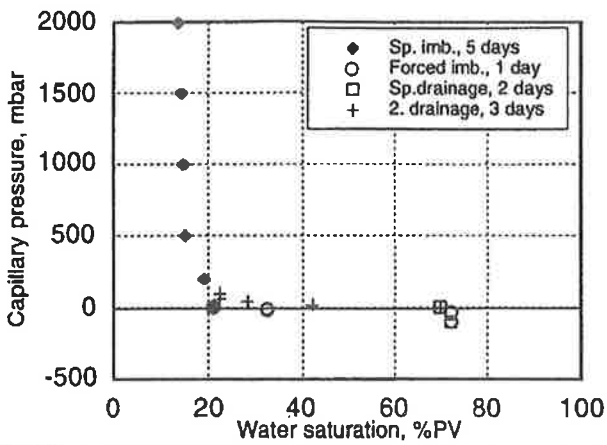

Figure 6: P_c loop (test #2), Vosges Sandstone, aged in crude oil, I_{HL} = 0.65

Discussion

The aged carbonate core (Fig. 8) was cleaned gently and resaturated (procedure 1) before the P_c curves were measured. Compared with the aged carbonate core from the Amott-IFP test (Table 2) which was not cleaned after aging (procedure 2), we see a difference in wettability index (comparing all three indices) towards a more oil-wet core when following procedure 2.

The aged sandstone (Fig. 6) and the core used in the Amott-IFP test both followed aging procedure 2. The difference between the three indices for experiment 2

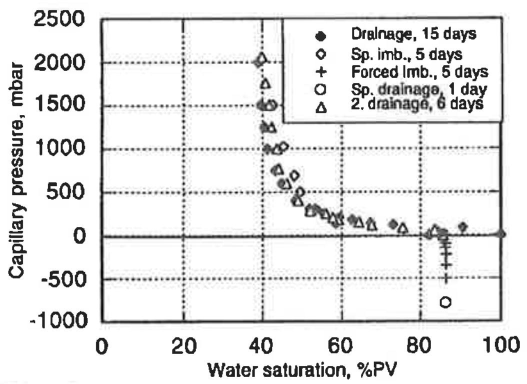

Figure 7: P_c loop (test #3), carbonate core, water-wet, I_{HL} = 0.97.

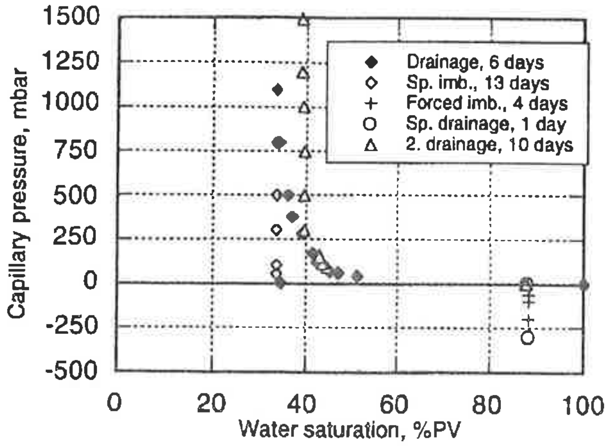

Figure 8: P_c loop test (test #4), carbonate core, aged in crude oil, I_{HL} = -0.01.

may be due to membrane damage since the secondary drainage curve had to be stopped at 100 mbar. Area A_1 is therefore cropped and the HL-index too high.

The sandstone core, from the Amott-IFP test, is still water-wet after aging, in agreement with the HL-index, while the other two indices indicate a neutral core. According to most tests, the carbonate core is easier to make oil-wet than the sandstone core, but the gentle cleaning procedure evidently affects wettability in a less oil-wet direction. The scale for the Amott indices and the HL-index is the same, from -1 to +1. For the USBM index the scale is from -∞= to +∞, in practice from -2 to +2, and can therefore not be compared directly with the other indices.

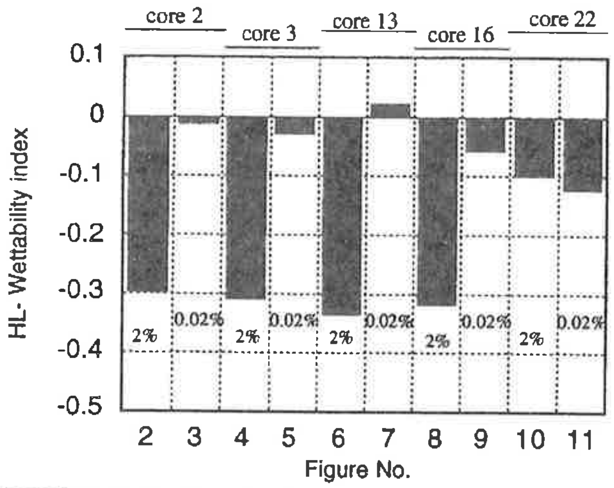

Figure 9: HL-indices from Gatenby and Marsden (1957).

In a paper by Gatenby and Marsden (1957), a whole loop of P_c curves was measured on five cores treated with two different concentrations of silicone CDri-film); 2% and 0.02%, giving ten P_c loops altogether. The HL-index has been calculated based on the figures in the paper using the weight of the areas cut in paper and measured on a micro balance. For the cores treated with a concentration of 2% silicone, the HL-index was around -0.3, except for core 22. For cores treated with a concentration of 0.02% silicone, the HL-index was around 0.0, except for core 22 (see Fig. 9). The Amott index has also been calculated based on the figures in the paper. Fig. 10 shows a comparison between the HL-index and the Amott index where data from both the paper by Gatenby and Marsden (1957) and from Table 2 are used. The results in Figs. 9 and 10 support the applicability of the HL-index.

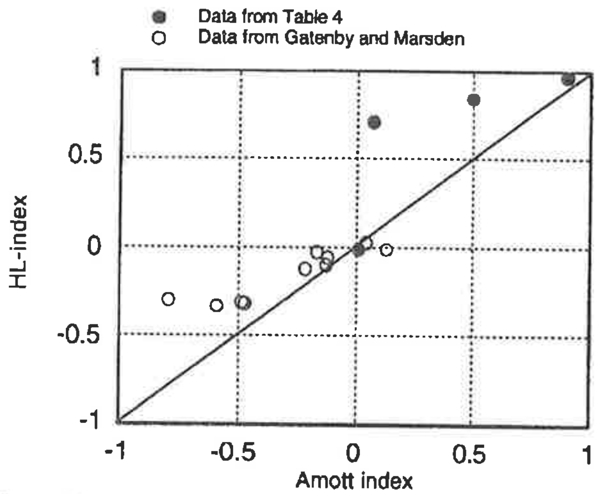

Figure 10: HL vs. Amott index.

Calhoun (1951) states that the entire P_c sequence should be used as a measure of wettability, by comparing the P_c curves. Gatenby and Marsden (1957) suggested the possibility of correlating wettability with the area of the hysteresis loop or other areas between the capillary pressure curve and the saturation axis. Morrow (1970) states that wettability of a porous medium relates to the surface energetics of displacement, but is not a well-defined term, and Brown and Neustadter (1980) suggest that the definition of the term wettability requires reference to the total system of solid plus fluids considered together with the kinetics of the displacement.

We suggest that the term wettability should express the overall tendency of a fluid spontaneously to imbibe as compared with its susceptibility to forced imbibition, when the whole saturation range is covered. More precisely, how much energy is released during spontaneous imbibition as compared with what is stored during forced imbibition. By this definition, the wettability is not a function of saturation, but an overall tendency of a reservoir rock to prefer one fluid over another.

For a reversible process, the area under the P_c curve, i.e.

$$\int P_c dS_w \qquad \ldots\ldots\ldots\ldots\ldots\ 4$$

is equal to the amount of free energy the core-fluid system may exchange with its surroundings (Morrow, 1970). The integral is negative when the system energy is increased and positive when energy is transferred to the surroundings.

Starting at irreducible water saturation (Fig. 2) for a water-wet core, spontaneous imbibition down to zero P_c results in release of stored energy equal to B_1. Next, forcing water into the core, the area A_2 (considered a positive quantity) is equal to the energy stored by the system, for a reversible process. The sum $B_1 + A_2$ is the total energy transfer over the saturation range and will be used as a normalizing quantity. Area B_1 represents the "suction energy" or potential energy stored because water is the wetting fluid. The energy of the rock-fluid system is lowered by this amount when water imbibes. Likewise, the area B_2 represents the energy released by spontaneous imbibition of oil.

If no Haines jumps take place, hysteresis is absent (Morrow, 1970) and the complete cycle of drainage and imbibition is reversible. (This would for instance be the case for pore channels that are conical in shape, without any restricting pore throats.) Then $A_1 = B_1$, $A_2 = B_2$, $I_w = A_1/(A_1 + A_2)$, $I_o = A_2/(A_1 + A_2)$, and the new wettability index for the reversible case is $I_{HL} = (A_1 - A_2)/(A_1 + A_2)$, i.e. the normalized difference between energies released by spontaneous imbibition of water and oil, respectively.

In an actual core, the pore channels form bodies and throats and the P_c curve will exhibit a hysteresis loop. As for ferromagnets (Feynman *et al.*, 1966) the area of the loop is equal to the energy lost, ultimately as heat, per cycle, caused by irreversible Haines jumps. In this case $A_1 \neq B_1$ and $A_2 \neq B_2$ and the new index is defined by Equations 1-3. By this choice, the definition is an extension of the Amott index, with the saturation intervals replaced by the corresponding integrals or energies.

In a recent paper by Toledo *et al.* (1994) it is shown by Monte Carlo simulations of volume-controlled mercury porosimetry of biconal pore segments that the area of the hysteresis loop depends on the aspect ratio, the ratio between the size of a pore body and a throat. A large contrast between body and throat results in more pronounced Haines jumps and energy losses. Therefore, if the HL-index is measured, it should be possible also to interpret the shape and area of the hysteresis loop to find descriptive parameters of the pore network.

So far we have not checked the reproducibility of the hysteresis loop, but we note from the work by Radke *et al.* (1992) that the wettability may change depending on the maximum (and minimum) P_c for a loop. Therefore, to reproduce the wettability index I_{HL} and the hysteresis loop, the minimum and maximum P_c probably need to be kept fixed at relevant limits for field operations.

Conclusions

1. The micropore membrane technique for P_c measurements is demonstrated to be an accurate and reliable method. Mercury injection (scaled) and traditional porous plate drainage curves show very good agreement with the membrane data.
2. The reduction in experimental time for this new technique with micropore membranes and reduced length of the core, is significant (30 times faster than standard porous plate).
3. A full cycle of P_c curves (four curves subsequent to primary drainage) has been obtained for water-wet and intermediate-wet cores within 20-30 days. The shape of the P_c curves for different core samples reflects the wettability of the core.
4. A new wettability index is suggested that takes into account the areas of the four P_c curves defining the hysteresis loop. The index may better quantify the wettability of a sample and discriminate between intermediate-wet, mixed-wet, and spotted-wet conditions.

References

Amott. E.: "Observations Relating to the Wettability of Porous Rock," *Trans. AIME* (1959) **216**:156-162.

Brown, C.E., and Neustadter, E.L.: "The Wettability of Oil/Water/Silica Systems with Reference to Oil Recovery," *J.Cdn.Pet.Tech.*, (July-September, 1980) Montreal, 100-110.

Calhoun, J.C.: "Criteria for Determining Rock Wettability," *Oil & Gas Journal* (May 10, 1951) **50**(1):151.

Cuiec, L.E.: "Evaluation of Reservoir Wettability and Its Effect on Oil Recovery," *Interfacial Phenomena in*

Petroleum Recovery, Morrow, N.R, (ed.), Surfactant Science Series, Marcel Dekker, Inc., New York (1991) **36**:334-6.

Donaldson, E.C., Thomas, R.D., and Lorenz, P.B.: "Wettability Determination and Its Effect on Recovery Efficiency," *SPEJ* (March 1969) 13-20.

Feynman, R.P, Leighton, R.B., and Sands, M: *The Feynman Lectures on Physics,* Volume II, Addison-Wesley, Reading, Massachusetts (1966).

Gatenby and Marsden: "Some Wettability Characteristics of Synthetic Porous Media," *Producers Monthly* (Nov. 1957) **22**(1):512.

Guo, Y. and Hammervold, W.L.: "Equilibrium Time and Accuracy of Capillary Pressure Measurement Using Diaphragm Method," paper presented at the 1993 SPWLA Annual Symposium, Calgary, June 13-16.

Hammervold, W.L. and Skjæveland, S.M.: "Improvement of Diaphragm Method for Capillary Pressure Measurement with Micro Pore Membrane," *Advances in Core Evaluation 111,* Worthington, P.F. and Chardaire-Riviere, C. (eds.), Gordon and Breach Science Publishers, (1992) 91-111.

Morrow, N.R.: "Physics and Thermodynamics of Capillary Action in Porous Media," *Ind. & Eng. Chem.* (June 1970) **62**(6):32-56.

Omoregie, Z.S.: "Factors Affecting the Equivalency of Different Capillary Pressure Measurement Techniques," paper SPE 15384 presented at the 1986 SPE Annual Technical Conference and Exhibition, New Orleans, Oct. 5-8.

Radke, C.J., Kovscek, A.R., and Wong, H.: "A Pore-Level Scenario for the Development of Mixed-Wettability in Oil Reservoirs," paper SPE 24880 presented at the 1992 SPE Annual Technical Conference and Exhibition, Washington, DC, Oct. 4-7.

Toledo, P.G., Scriven, L.E. and Davis, H.T.: "Pore-Space Statistics and Capillary Pressure Curves From Volume-Controlled Porosimetry," *SPEFE* (March 1994) 46-54.