EVALUATION OF WETTABILITY DISTRIBUTIONS IN EXPERIMENTALLY AGED CORE

Else Johannesen[1], James Howard[2] and Arne Graue[1]
[1]University of Bergen, Bergen, Norway
[2]ConocoPhillips, Bartlesville, OK, USA

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Abu Dhabi, UAE 29 October-2 November, 2008

ABSTRACT
There are a number of laboratory procedures to alter or restore wettability to its original state after cleaning. It is important with these methods to establish a uniform distribution of wetting states in the core prior to SCAL testing. Earlier efforts to evaluate in-situ wettability distribution in samples aged under different procedures were based on spatial distribution of water imbibition and waterflooding to obtain a local Amott index. The local fluid saturation development was obtained by MRI or nuclear tracer techniques. Previous work has demonstrated relationships between NMR relaxation times of water and oil components that saturate a core and the wettability of the sample. NMR T_2 measurements made in the presence of a fixed magnetic gradient field along the core's longitudinal axis result in transverse slices of relaxation time distributions. The results may be used for 1D fluid saturation imaging purposes and local relaxation time-based wettability determination.

Four core plugs were aged at elevated temperature using different methods; submersed in oil and by uni-directional and multi-directional flooding procedures. NMR T_2 measurements obtained during a subsequent spontaneous brine imbibition showed distinct differences between core plugs aged differently with respect to the distribution of water saturation and relaxation time-based wettability indices, henceforth denoted T_2 Wettability. Samples aged in an oil bath had lower wettability indices in both ends. Samples prepared by flooding the crude oil in one direction had a narrower range of water saturation and wettability indices with a slight trend of increasing water wetness towards the outlet end. Samples prepared by multi-directional flooding of the crude oil had the most uniform distributions of water saturation and T_2 Wettability. For all samples the local Amott indices and the T_2 Wettability correlated well.

INTRODUCTION
Earlier studies have shown that low field NMR spectroscopy provides potentially a quantitative and fast in-situ technique for determining reservoir wettability (Howard and

Spinler, 1995, Howard, 1998, Fleury and Deflandre, 2003, Looyestijn and Hoffman 2005, Johannesen *et al*., 2006 and 2007a). The technique uses the sensitivity of a low field NMR spectrometer to determine the fluid distribution in oil- and water-saturated core plugs. The interpretation model is based on the existence of a surface relaxivity for both oil and water, allowing determination of the amount of surfaces wetted by either oil or water.

The important features of a pore may be divided into its surface area S and bulk volume V. The NMR-sensitive surface area is a thin layer of a few molecules close to the pore wall surface, and the bulk volume is the rest of the pore volume that usually dominates the overall pore volume. T_2 relaxation time is significantly faster for a molecule in the surface area, compared to a molecule in the bulk area. This is an effect of paramagnetic centres in the pore wall surface that cause the relaxation time to be faster (Brown and Fatt, 1956).

The inverse of the measured relaxation time (or rate), T_i, is a combination of contributions from the bulk area V, the surface area S and the self diffusion d

$$\frac{1}{T_i} = \left(1 - \frac{\delta \cdot S}{V}\right)\frac{1}{T_{ib}} + \frac{\delta \cdot S}{V}\frac{1}{T_{is}} + \frac{(\gamma G t_E)^2 D}{12} \quad i=1,2 \tag{1}$$

where δ is the thickness of the surface area, S is the surface area, V is the pore volume, T_{ib} is the relaxation time for bulk, T_{is} is the relaxation time for the surface, γ is the gyromagnetic ratio, G is the magnetic field gradient (assumed to be constant), t_E is the time between echoes and D is the self diffusion coefficient of the fluid.

In a T_2 distribution plot, the amplitude of the signal is proportional to the total amount of hydrogen nuclei, and the relaxation time depends on the nuclear spins surroundings. In a pore containing i.e. water, the bulk water exhibits a single exponential decay. The water close to the pore wall surface provides an additional relaxation time, resulting in a faster observed T_2 relaxation time for this characteristic pore size:

$$\frac{1}{T_i} \approx \rho \frac{S}{V} \tag{2}$$

where ρ is the surface relaxivity defined as:

$$\rho = \frac{\delta}{T_{iS}} \tag{3}$$

T_2 relaxation time will be faster for smaller pores and longer for larger pores. Therefore, the *S/V* ratio is a measure of pore size.

The reported experiments were fitted with non-linear optimization algorithms that used multi-exponential terms to separate the water phase from the oil phase (Howard and Spinler, 1995):

$$M(t) = \sum_{i=1}^{n} V_i \exp(-t / T_{2i}) \tag{4}$$

where $M(t)$ is the echo amplitude at time t, T_{2i} is the relaxation times for water and oil and V_i is the volume fractions of oil and water. Advantage of the multi-exponential fitting is that it allows one to predetermine a larger number of T_2 terms that cover the range of interest.

Earlier reported results on Portland chalk and Edwards limestone indicated a linear relation between wettability determined by the Amott test and T_2 relaxation time for the oil phase at irreducible water saturation, S_{iw} (Johannesen, 2006 and Johannesen, 2007). The CPMG sequence was used for measurements of T_2 distributions. In a uniform magnetic field, B_0 (Figure 1a), T_2 relaxation times for the oil phase decreased with decreasing wettabilities in Portland Chalk samples as reflected by Amott indices.

For some instances it may be desirable to measure wettability in parts of a core plug or to find the saturation or the wettability distribution in the core. In a low field NMR instrument with gradient coils it is possible to measure relaxation times in transverse slices at different thicknesses and positions. To obtain transverse slice measurements the magnetic field, B_0, is supplemented by gradient coils establishing a static linear gradient field (Figure 1b). With such a gradient applied along the longitudinal axis of the core plug, the resonance frequency of the hydrogen protons in the core plug is varied in a linear fashion. Selected nuclei in transverse slices at the given frequency can then be measured.

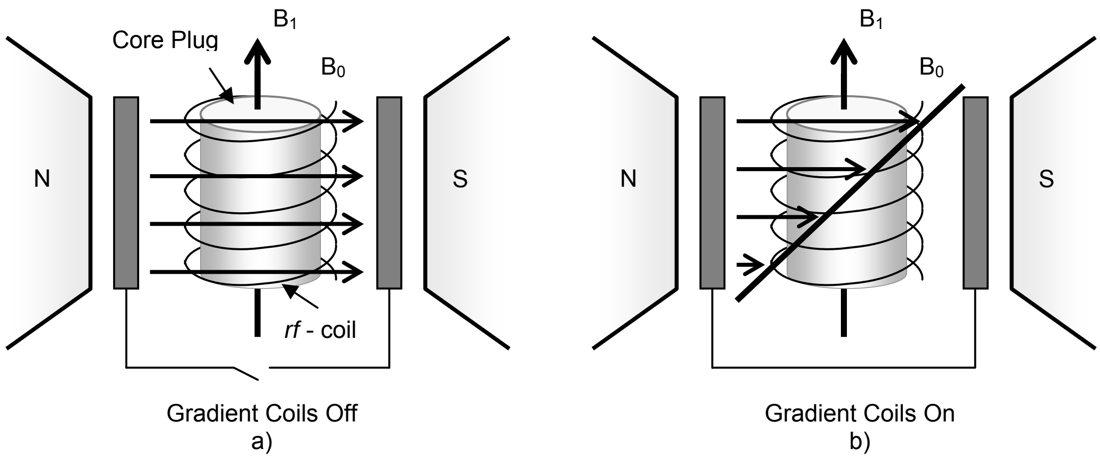

Figure 1. A core plug in a) a uniform magnetic field, B_0, b) a gradient magnetic field, B_0.

To excite a single slice along the axial length of a core plug, radio waves of the relevant frequency, *f*, can be generated, as dictated by

$$f = \gamma \cdot B_0 \qquad (5)$$

where γ is the gyromagnetic ratio.

Both the strength of the gradient field and the bandwidth of the *rf*-pulse influence the thickness of the selected slice. In the reported work the frequency is kept constant, but the gradient field is varied to obtain measurements from transverse slices of different thicknesses (Figure 2a). If the gradient field is low (B_{0a}) the transverse slice is thick (Δy_a). The slice thickness (Δy_b) decreases as the gradient field increases (B_{0b}). For a slice in the middle of the gradient field the frequency offset is 0. To measure slices at various positions along the longitudinal axis of a core plug, the frequency offset is changed either over or under 0 to a given position (Figure 2b).

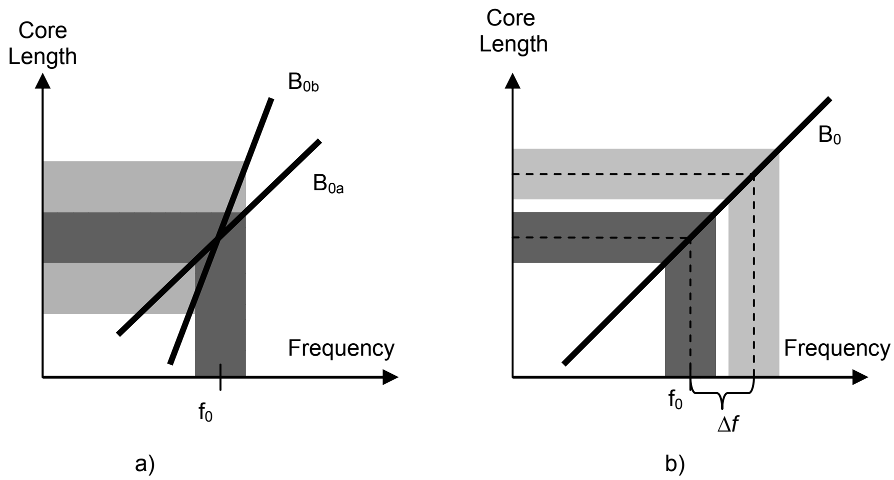

Figure 2. Effects on gradient field and slice thickness (a) and frequency and slice offset (b).

EXPERIMENTAL PROCEDURES

Core Plugs

Core plugs were cut from several blocks of Rørdal chalk obtained from the Portland quarry at Ålborg in Denmark. The cores were cut to a length and diameter of 6 cm and 3.8 cm, respectively. The core plugs were dried in an oven at 90°C for at least two days. The dry core plugs were evacuated and saturated with brine. Porosity was determined by mass balance calculations. The absolute permeability to water was determined with Darcy's law by measuring pressure differences across the sample at constant injection rate.

Fluids

Two different crude oils denoted D and H were used as the oil phases in the aging process. A summary of the crude oil characterizations is given in Table 1. Data on the synthetic formation brine, decalin and decane used in the experiments is given in Table 2.

Table 1. Results from crude oil analysis.

Oil	Acid#	Base#	IEP	μ 20°C [cP]	ρ_D 20°C [g/ml]	Molecular Weight [u]	RI 20°C	API 20°C	Sat %	Asp %	Res %	Aro %
D	0	0.11	4.3	2.06	0.794	171	1.446	46.7	82.6	0.008	2.54	14.80
H	0.09	1.18	-	14.3	0.85	-	-	-	53	0.90	12	35

Table 2. Brine and mineral oils.

Fluid	Type/Content	Viscosity at 20°C [cP]	Density at 20°C [g/cm^3]
Brine/Water	Distillate water 5 wt. % NaCl 3,8 wt. % $CaCl_2$ 0.01 wt. %NaN_3	1.057	1.09
n-Decane ($C_{10}H_{22}$)	Mineral oil	0.73	0.92
Decahydronaphtalene (Decalin, $C_{10}H_{18}$)	Mineral oil	0.90	0.85

Wettability Alteration
This paper focuses on wettability distributions in core plugs using different aging methods. Four different aging methods were used. In the following each method is described in detail.

Method 1
Method 1 is based on the work of Aspenes *et al*. (2003). Improved laboratory equipment gave the opportunity for further improvement of this aging technique (Johannesen *et al*. 2007b).

Core plugs were drained to S_{wi} with crude oil at constant pressure (2 bar/cm) at elevated temperature (80°C). This included crude oil flow in both directions to reduce saturation gradients caused by capillary end effects. Produced water and crude oil was accumulated. After drainage, the aging process started by injecting crude oil through the core plug at the constant flow rate of 1.5 ml/h. To obtain a uniform wettability distribution, the flow direction of the crude oil was reversed after half aging time.

After completed aging 5 PV of decalin was injected through the core plugs from both directions. Decalin was used to prevent destabilization of the crude oil. Then, 5 PV of decane was fluhed through the core plugs. Decane was used to establish a stable and reproducible fluid rock system with a similar mobility ratio at room temperature as experienced in a chalk reservoir under study at elevated temperature.

Method 2
Method 2 is similar to Method 1, but the flow direction during drainage and aging was not reversed. Decalin and decane were injected as for Method 1. The purpose of this method was to study if aging from only one direction would give a non-uniform wettability distribution.

Method 3
Core plugs were drained with ½ PV from only one end and then aged in the core holder at static conditions at elevated temperature (80°C). Decalin and decane were injected as for Method 1. The purpose for this method was to establish core plugs with strongly water-wet conditions in one end and less water-wet conditions in the other end.

Method 4
The aging technique used in Method 4 is described by Zhou *et al.* (2000). Core plugs were drained with crude oil to S_{wi} from both ends. Then, the core plugs were submerged in an oil bath covered with aluminium foil to minimize evaporation of the light components in the crude oil. The core plugs submerged in crude oil were aged in an isolated cabinet

holding 80°C. As opposed to the work of Zhou *et al.* (2000), the crude oil in these cores was replaced by decalin and decane as described in Method 1. This exchange of the oil phase was performed to ensure that the wettability alteration process stopped after completed aging. The purpose of this method was to study the uniformity of the wettability in core plugs aged using this technique.

Determination of Wettability Distribution by NMR Gradient Measurements

Several instrument parameters need to be investigated to obtain an optimal T_2 signal from a NMR measurement on chalk. Chalk has mainly one pore size (Reppert, 2006), and the pores are also relatively small. Diffusion is therefore not distinctive in this rock type and TAU, τ, was set to 500 µs. To ensure that all slow components relaxed, the number of echoes (NECH) was set to 4096 so that the total length of the experiment exceeded the relaxation times for bulk decane and brine. The signal to noise (SNR) increases when numbers of scan (NS) increases. In the reported work NS was 64. Relaxation Delay (RD) was set to 6 s to ensure full polarization between each CPMG sequence.

CPMG Gradient measurements were performed on four transverse slices with thickness of 1 cm each, as illustrated in Figure 3. Two slices had positive and negative offset of 0.5 cm and two slices had positive and negative offset of 1.5 cm. CPMG Gradient measurements were performed at irreducible water saturation, S_{iw}, at end point water saturation after spontaneous imbibition of water, S_{wsp}, and at water saturation after forced waterflood, S_{wor}. The NMR Gradient technique was used for both T_2 Wettability determination (T_2 relaxation time for the oil phase at S_{iw} divided by T_2 relaxation time for the oil phase at S_{iw} for a strongly water-wet core) and saturation distribution measurements so that local Amott indices could be calculated.

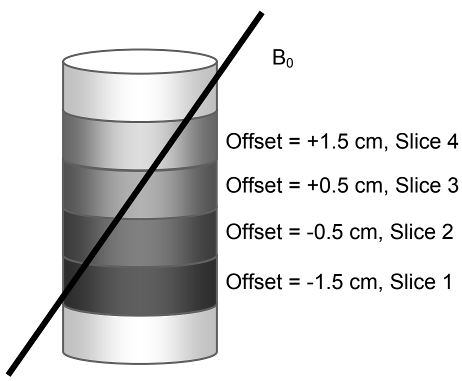

Figure 3. Four transverse slices during CPMG gradient measurements. All slices were 1 cm.

RESULTS AND DISCUSSIONS

The longitudinal T_2 relaxation time and saturation distribution in four core plugs aged using the four different methods described above was measured. Core plug data are given in Table 3.

Table 3. Core plug data

Core Plug	Porosity	Permeability [mD]	Aging Technique	Crude oil	Aging Time
G25	0.47	4.8	Method 4	H	10 days
G23	0.45	3.8	Method 2	H	10 days
G10	0.48	5.1	Method 3	H	8 days
E10	0.46	4.2	Method 1	D	4 days

Core Plug G25, presented in Figure 4, was aged by submergence in an oil bath at elevated temperature (80°C) for 10 days. Both the trend curves for Amott Index and T_2 Wettability indicate that the core plug has undergone more wettability changes in each end compared to the middle of the core. The heterogeneous symmetric wettability distribution along the longitudinal axis of the core may be explained by the aging technique performed on this core plug. More diffusion of crude oil has occurred in pores located close to the surface of the core plug, and the wettability is then expected to change more in these pores compared to pores in the middle of the core plug where less diffusion of oil has occurred. The outer layer might appear as a barrier for the water to imbibe into the core plug, and therefore give an apparently lower wettability reflected by Amott Index compare to the T_2 Wettability. T_2 Wettability is a measure of the oil film thickness, δ, at the pore wall surfaces, and should then be more proper as a measure of wettability for core plugs aged using Method 4. The results corroborate results reported by Spinler *et al.* (2002), and Graue *et al.* (2002).

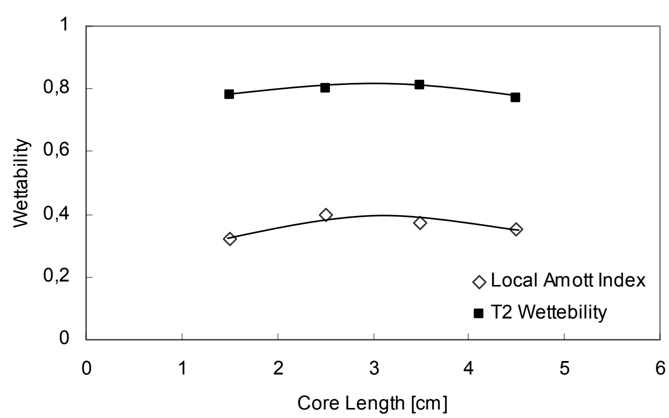

Figure 4. T_2 Wettability and Amott Index wettability as a function of core length for Core Plug G25.

Core Plug G23 (Figure 5) was aged in 10 days using Method 2. The core plug was drained by crude oil H to S_{wi} from both ends and then aged with a constant flow rate (1.5 ml/h) in only one direction, from left to right (inlet to outlet). The purpose of this experiment was to investigate how much the oil flow direction during aging affects the longitudinal wettability distribution. Both the T_2 Wettability and the Amott Index trend curves show that the core plug has undergone more wettability alteration in the inlet end. Results are similar to earlier reports in the literature (Graue *et al.* 2002). The Amott Index trend curve shows completely neutral wet conditions at the inlet end, and the wettability increase to about I_w = 0.3 at the outlet end.

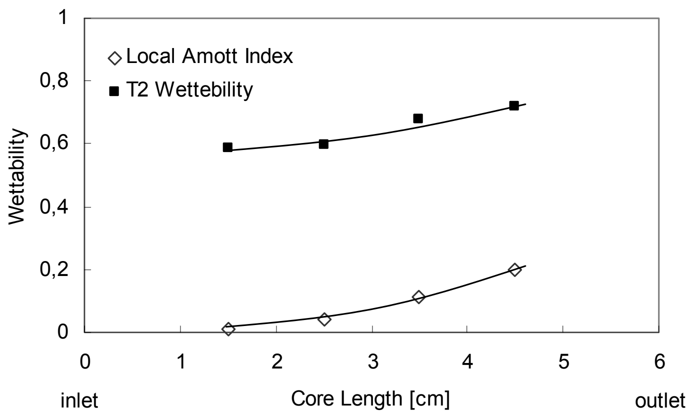

Figure 5. T_2 Wettability and Amott Index wettability as a function of core length for Core Plug G23.

Core Plug G10 was aged for 8 days using Method 3. The core plug was drained with only ½ PV of crude oil. The purpose of this experiment was to make a wettability gradient along the longitudinal axis of the core plug. With an axial saturation gradient along the core, the new established wettability distribution was expected to appear as a gradient, because a larger fraction of pore wall surface was exposed to crude oil in the inlet end. Figure 6 shows that the core plug has undergone more wettability alteration in the inlet end (crude oil was injected from left). The Amott Index trend curve shows neutral wet condition in the inlet end and the longitudinal wettability increases gradually to nearly strongly water-wet in the outlet end. The T_2 Wettability trend curve has the same shape as for the Amott Index trend curve, but the slope is not as steep.

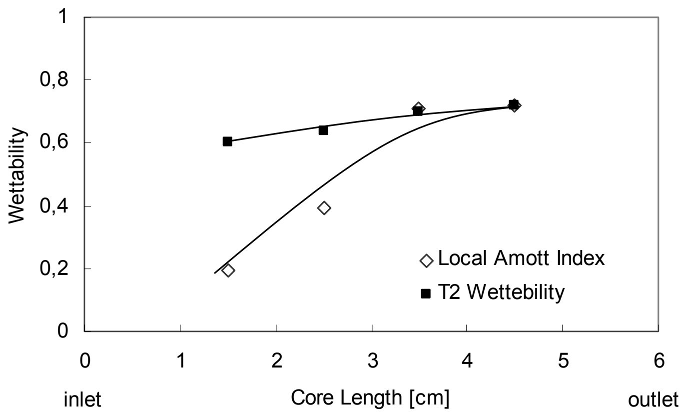

Figure 6. T_2 Wettability and Amott Index wettability as a function of core length for Core Plug G10.

Core Plug E10 (Figure 7) was aged in 4 days using Method 1. Both the T_2 Wettability and the Amott Index trend curves show an almost uniform wettability distribution along the longitudinal axis of the core plug. This corroborates findings reported by Aspenes *et al.* (2003).

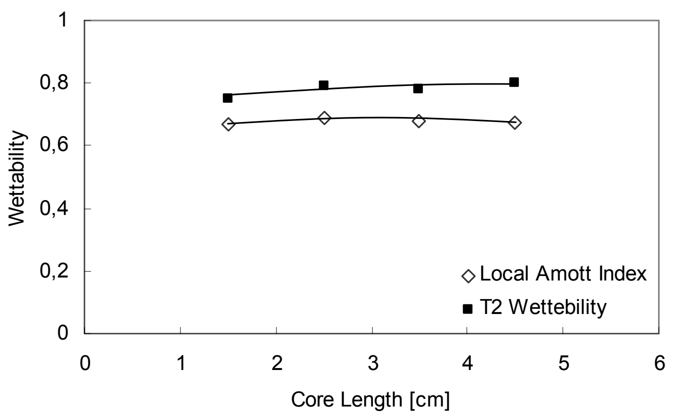

Figure 7. T_2 Wettability and Amott Index wettability as a function of core length for Core Plug E10.

The CPMG gradient results from Figures 4, 5, 6 and 7 are plotted as Amott Indices versus T_2 Wettability and compared to the CPMG results from a uniform magnetic field reported by Johannesen *et al*. (2006). All CPMG gradient results are close to the CPMG uniform magnetic field trend curve. This indicates that the CPMG gradient measurements can be used for longitudinal saturation and wettability distribution in homogeneous chalk core plugs.

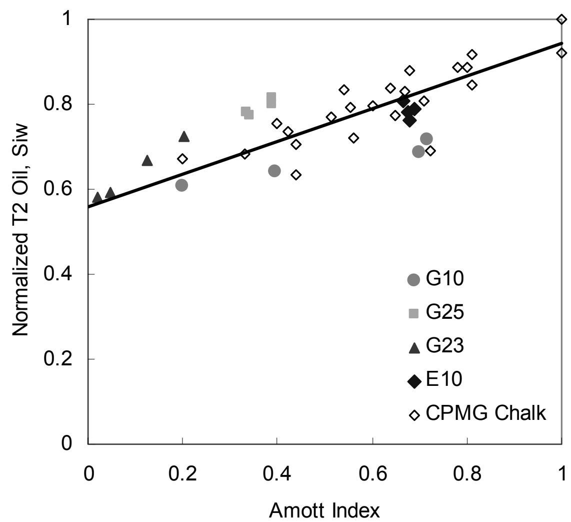

Figure 9. Amott Index versus T_2 Wettability for the CPMG measurements presented in Figure 1 and for the CPMG gradient measurements presented in Figures 5, 6, 7 & 8.

CONCLUSIONS

The results corroborate earlier reports of NMR measurements indicating a linear relationship between wettability and T_2 relaxation times for the oil phase in chalk core plugs. T_2 relaxation time for the oil phase at irreducible water saturation, S_{iw}, decreased with decreasing wettability; reflected by the Amott indices.

Axial saturation and wettability distributions have been determined by NMR T_2 measurements in chalk core plugs. Different aging techniques have been tested and shown to give various degrees of uniformity in the axial distributions. An improved aging technique with multidirectional flooding during aging gave the most uniform wettability distribution.

The CPMG gradient technique may be used for axial in-situ saturation and wettability determination.

NOMENCLATURE

D = self diffusion coefficient of fluid, cm^2/s
G = magnetic field gradient, gauss/cm
$M(t)$ = echo amplitude
B_{0a} = low field gradient
Δy_a = slice thickness, low field gradient
Δy_b = slice thickness, high field gradient
B_{0b} = high field gradient
PV = pore volume
I_w = Amott index to water
S_{iw} = irreducible water saturation
S_{wi} = initial water saturation
S_{wsp} = water sat. after spontaneous imbibition
S_{wor} = water sat. after forced waterflood
S = pore surface area, m^2
T_2 = spin-spin relaxation time, s
T_{ib} = relaxation time for pore bulk, s
T_{is} = relaxation time for pore surface, s
t = time, s
t_E = time between echoes, s
V = pore volume, m^3

V_i	=	volume fraction of pore size i	Asp	=	Asphaltenes
δ	=	thickness of pore surface area	Res	=	Resins
γ	=	gyromagnetic ratio, Mhz/T	Aro	=	Aromatics
ρ	=	surface relaxivity	API	=	American Petroleum Institute gravity
ρ_D	=	Density, g/ml	μ	=	viscosity, cP
RI	=	Refractive Index			
Sat	=	Saturates			

REFERENCES

- Amott, E.: “Obervations Relating to the Wettability of Porous Rock”, *Trans., AIME* (1956) **216**, 156.
- Aspenes, E., Graue, A., Ramsdal, J.: “In-Situ Wettability Distribution and Wetting Stability in Outcrop Chalk Aged in Crude Oil”, J. Pet. Sci. & Eng. 39 (337-350), 2003.
- Brown, R.J.S., Fatt, I., “Measurements of Fractional Wettability of Oilfield Rocks by the Nuclear Magnetic Relaxation Method”, (1956) *Trans. AIME*, **207**, 262-264.
- Dastidar, R., Sondergeld, C.H., Rai, C.S., “NMR Desaturation and Surface Relaxivity Measurements on Clastic Rocks” (2006) SPE 99629.
- Fleury, M. and Deflander, F.: “Quantitative Evaluation of Porous Media Wettability using NMR Relaxometry”, *Magnetic Resonance Imaging*, **21**, (2003) 385-387.
- Graue, A., Viksund, B. G., Baldwin, B. A., "Reproducible Wettability Alteration of Low-Permeable Outcrop Chalk." *SPE Reservoir Evaluation and Engineering*, (1999) **2**: 134-140.
- Graue, A., Aspenes, E., Bognø, T., Moe, R. W., Ramsdal, J., "Alteration Of Wettability And Wettability Heterogeneity." *Journal of Petroleum Science and Engineering*, (2002) **33**: 3-17.
- Hirasaki, G. and Zhang, D.L.: “Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formations”, SPEJ 88365, Jun., (2004).
- Howard, J.J., “Quantitative Estimates of Porous Media Wettability from Proton NMR Measurements”, (1998)
- Howard, J.J., Spinler, E. A., “Nuclear Magnetic Resonance Measurements of Wettability and Fluid Saturations in Chalk”, (1995) SPE 26471, Houston.
- Johannesen, E.B., Steinsbø, M., Howard, J.J. and Graue A., “Wettability Characterization by NMR T_2 Measurements in Chalk”, *International Symposium of the Society of Core Analysts, 12-16 September 2006, Trondheim, Norway*, (2006).
- Johannesen, E.B., Riskedal, H., Tipura, L., Howard, J.J. and Graue, A., “Wettability Characterization by NMR T_2 Measurements in Edwards Limestone Rock”, *International Symposium of the Society of Core Analysts, 10-13 September 2007, Calgary, Canada*, (2007).
- Looyestijn, W. and Hoffman, J.: “Wettability Index Determination by Nuclear Magnetic Resonance”, SPE93624, Bahrain, Mar., 2005.
- Reppert, M.G., Akkurt, R., Howard, J.J., and Bonnie, R.J.M., 2006, Porosity and water saturation from LWD NMR in a North Sea Chalk Formation, *Petrophysics,* v. 47, no. 5, p. 442-450.
- Spinler, E.A., Baldwin, B.A., Graue, A.: “Experimental Artifacts Caused by Wettability Variation in Chalk”, J. Petr. Sci.&Eng., Vol. 33, Nos. 1-3, (49-59), 2002.
- Zhou, X. and Morrow, N.R.: *“Interrelationship og Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibition and Waterflooding”*, *SPE Journal* (June 2000) **5**, 2.