WETTABILITY CHARACTERIZATION BY NMR T_2 MEASUREMENTS IN CHALK

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ABSTRACT
Nuclear Magnetic Resonance (NMR) T_2 relaxation properties for oil- and water-saturated outcrop chalk were measured using the CPMG sequence at various wettabilities and at various fluid saturations in order to their usefulness for wettability characterization. Slower T_2 relaxation times and increased intensity are associated with the water phase signal as the water saturation increases during spontaneous imbibition. The assumption that the shifts in the water phase T_2 relaxation time would decrease at less water-wet conditions due to reduced surface relaxation, and be a non-linear function of saturation was not corroborated. The relative shift for T_2 relaxation time for the oil phase during spontaneous imbibition as a function of increasing water saturation, S_w, was observed to consistently and gradually change from a shift toward slower relaxation for strongly water-wet conditions to a shift toward faster relaxation for more neutral wet conditions.

INTRODUCTION
The wettability conditions in porous media containing two or more immiscible fluid phases determine the microscopic fluid distribution in the pore network. NMR measurements are sensitive to wettability because of the strong effect that the solid surface has on promoting magnetic relaxation of containing fluid. The idea of using NMR as a tool to measure wettability started by Brown (1956) and is long established in the literature (ref. 1-9, 13-20, 22-28).

Because of advancements in low-field NMR technology and the interest in porous media in the 1990's, the amount of experimental data related to wettability and NMR research increased significantly. Howard and Spinler (1995) reported how multi-component fitting of the relaxation data reveals more information than the single- and stretched-exponential fitting used in the earlier studies. They compared NMR relaxation data measured on a large number of similar samples and demonstrated how the multi-component fits made it possible to interpret the abundance of both water and oil phases with proton measurements made in low field-strength spectrometers comparable to the fields used in this new generation of NMR logging tools. A model based on relative shifts of the T_1 relaxation for water component as a function of saturation was proposed for quantifying wettability changes in porous media by Howard and Spinler (1995) and Howard (1998). More recently, Looyestijn and Hofman (2005) published a work based on a model for the microscopic distribution of crude oil and water in a porous rock at any given overall saturation.

EXPERIMENTAL PROCEDURES

27 Rørdal outcrop chalk core plugs, representing porosity from 42 to 46% and permeabilities from 3.3 to 4.5 mD, were aged at S_{wi}, using alternate flooding from both ends with crude oil at elevated temperature, to obtain chalk core plugs at various wettabilities. The procedure is described by Graue *et al.* (1999, 2000). The crude oil used for aging was replaced by decane to establish a stable and reproducible fluid rock system, with a similar mobility ratio at room temperature as experienced in a reservoir at elevated temperature.

NMR T_2 measurements were obtained at end point water saturation after forced imbibition, S_{orw}, at non-reducible water saturation, S_{wi}, at different times during oil production by spontaneous water imbibition and at end point water saturation after spontaneous imbibition, S_{wsp}. To initiate the spontaneous oil production, the cores were placed in a water bath. During the spontaneous water imbibition, each core plug was taken out of the water bath at various selected times and placed in the NMR instrument to measure T_2 relaxation times. Before each NMR measurement the core was wrapped in a plastic foil to minimize evaporation. Thus, the T_2 relaxation times were measured at different water saturations, using the CPMG sequence. The fluid saturations were found by integrating the NMR response curves for each phase and normalize to the corresponding results at 100% saturations, and the saturation results were used to obtain the dynamics for the spontaneous imbibition.

The material balance data was obtained using results from the measurements of the T_2 relaxation times and from independent weight measurements. Both methods gave nearly the same saturation results. The material balance given in this report is from the NMR measurements.

T_2 relaxation time for the bulk water was measured to ca 2600 ms, and for bulk decane ca 1300 ms. We used decane instead of crude oil in this experiment to establish a stable wettability and to simplify the imbibition process. The T_2 measurements will not be affected of this simplification, because this only becomes an issue with higher viscosity oils (lower API numbers) when the T_2 relaxation time of the oil becomes faster and overlays the water relaxation peak.

EXPERIMENTAL RESULTS AND DISCUSSION

Microscopically the volume of a single pore in a porous rock may be divided into two regions; surface area S and bulk area V (Figure 1.). The surface area is a thin layer with thickness δ of a few molecules close to the pore wall surface. The bulk area is the rest of the pore volume that usually dominate the overall pore volume. With respect to NMR excitations of atomic states for hydrogen containing molecules in these regions, different relaxation times for the induced excited energy states are expected. The 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 causes the relaxation time to be faster, as reported by Brown (1956).

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

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

Impacts from Wettability on T_2 for the Water Phase

The main objective with these NMR-experiments was to determine if a shift in the T_2 relaxation times at various saturations was consistent with a change of the wettability. The proposed simple model suggests that a change in the saturation distribution within a single pore will cause a change in the relaxation times, e.g. in a oil-wet system the T_2 relaxation time for oil will decrease when S_o increases; as more oil will interact with the pore surface and thus cause the relaxation time for the oil to be faster. However, if the faster oil phase relaxation time is observed at lower oil saturation, it may indicate more oil-wet rock according to more dominant surface relaxation. Thus, a non-linear increase in the relative relaxation times as function of saturations may indicate a different wettability state. We anticipate therefore being able to obtain wettability information by the NMR T_2 relaxation measurements.

Figure 2 illustrates the NMR signal intensity as a function of T_2 relaxation time for a strongly water-wet core plug, I_w = 1.00. The two peaks at S_w=100% illustrate the pore size distribution. The largest peak, at T_2 about 40 ms is typical for T_2 – distributions for chalk, with a uniform and narrow pore size distribution. It is evident that surface relaxation is the dominating process in this instance, since T_2 relaxation time for bulk water is about 2600 ms. The small peak at T_2 about 200 ms indicates vugs in the core plug, and because of larger pore diameter in vugs the bulk relaxation is more predominating. Chalk has normally a uniform pore size distribution, and vugs are rare for this rock type, ref. Howard (1993). As water saturation increases during spontaneous water imbibition, the vugs containing fairly mobile oil will quickly be displaced and filled with water. The T_2 relaxation time at each fluid saturation is found by adjusting a 3rd degree polynomial function to the T_2 peak and deriving the function. From Figure 2 it can be seen that the T_2 relaxation time for the water phase (between 10 and 100 ms) increases with increasing water saturation, as the bulk water contribution gets more dominating. The signal intensity is also increasing because of increasing water saturation.

Impacts from Wettability on T_2 for the Oil Phase

<u>Strongly Water-wet Conditions</u>

In **Figure 2** the T_2 peak for the oil phase is found to be about 1000 ms. The shift in T_2 relaxation time for the oil phase is not as significant as for the water phase, but a small shift toward slower relaxation is observed, indicating a consistent increase in T_2 with increasing water saturation. The signal intensity for the oil peaks is decreasing during spontaneous imbibition, as expected because of less bulk oil contribution. Because no water production was recorded during forced imbibition the T_2 peaks for the oil phase at S_{wsp} and S_{orw} are about the same.

Moderately Water-wet Conditions

The relative shift in T_2 relaxation time for the oil phase as a function of water saturation at various wettabilities is illustrated in Figure 3. The figure illustrates that the relative shift in the T_2 relaxation time for oil during spontaneous imbibition depends on the wettability conditions. At strongly water-wet conditions T_2 for oil increases with increasing water saturation but the relative increase starts to decline as the Amott Index decreases. At a wettability of about $I_w = 0.60$ no relative shift in T_2 is observed, followed by a trend of decreasing T_2 values at less water-wet conditions when water saturation is increased. It is also observed that at the end point water saturation after forced imbibition (S_{orw}) the T_2 peak has a significant lower value compared to the spontaneous imbibition saturation range (Figure 6).

Weakly Water-wet Conditions

When the Amott Indices indicate weakly water-wet conditions, the trend line for the relative shift in T_2 for the oil phase has a negative gradient during spontaneous imbibition (Figure 3). The development of T_2 relaxation time for a weakly water-wet core plug as water saturation increases during spontaneous imbibition is shown in Figure 4. A small shift in T_2 for the oil phase toward faster relaxation time is observed during spontaneous water imbibition, indicating that the T_2 for oil at S_{orw} is shorter than for S_{wi} and S_{wsp} (Figure 6). The development of the trend lines of relative shift in T_2 relaxation time for the oil phase for all core plugs shown in Figure 3 are illustrated in Figure 5 as a function of the Amott Index.

Discussion of the T_2 Shift for the Oil Phase as a Function of Wettability

The fact that the gradient of the trend lines shown in Figure 5 turns to be negative at about $I_w = 0.60$ may be explained as a pore surface to volume phenomenon. From equation (1) we see that S/V-ratio is proportional to $1/T_2$

$$\frac{S}{V} \sim \frac{1}{T_2} \tag{2}$$

For the strongly water-wet condition this indicates that at S_{wi} some oil is in close contact with the pore wall, the surface relaxation is dominating and the T_2 relaxation time is shortened (Figure 8a). At S_{wsp} T_2 relaxation time increases to a value close to T_2 relaxation time for bulk decane (1300 ms). This means that all residual oil is located in the central part of the pore, and the dominating bulk relaxation brings a positive gradient (Figure 5).

For the moderately water-wet conditions some oil has wetted the pore wall, and the surface relaxation contributes to the S/V-ratio at S_{wi} (Figure 8b). After spontaneous imbibition, at S_{wsp}, the oil volume in the pore is reduced and as the water imbibes along the pore wall less oil is in contact with the surface. Surface relaxation and bulk relaxation will decrease accordingly during spontaneous water imbibition and the T_2 relaxation time remains constant (Figure 5).

When the wettability is weakly water-wet more of the pore wall is wetted by the oil (Figure 8c). Because of less spontaneous imbibition at this wettability condition, with a larger contact angle between the pore surface and the oil, the surface contribution will be less affected. But the reduced bulk volume will reduce the S/V-ratio during spontaneous imbibition, and result in a negative gradient (Figure 5). From weakly water-wet to neutral wet the gradient curve (Figure 5) is flattening off because of almost no spontaneous imbibition at this wettability.

In Figure 7 the residual oil saturation at S_{orw}, is plotted as a function of Amott Index for all core plugs. The plot shows an optimum oil recovery when the wettability is about I_w = 0.4 as expected, ref. Morrow (1990). The shape of the curve in Figure 7 resembles the shape of the S_{orw}–curve in Figure 6.

CONCLUSION

- A consistent shift toward slower T_2 relaxation times for the water phase was observed at increasing water saturations.
- The relative shift for T_2 relaxation time for oil during spontaneous imbibition as a function of increasing water saturation was observed to consistently and gradually change from a shift toward faster relaxation at strongly water-wet conditions to a shift toward slower relaxation for more neutral wet conditions.
- The residual oil saturation was observed to have a minimum value when the wettability was about $I_w = 0.4$.

Nomenclature

D	= self diffusion coefficient of a fluid, cm^2/s	T_1	= spin-lattice (longitudinal) relaxation time, s
G	= magnetic field gradient, gauss/cm	T_2	= spin-spin relaxation (transverse time, s
I_w	= Amott Index (wettability index)	T_{ib}	= relaxation time for pore bulk, ms
S_w	= water saturation	T_{is}	= relaxation time for pore surface, ms
S_{or}	= residual oil saturation	t_E	= time between echoes, ms
S_{wi}	= non- reducible water saturation	V	= pore volume, m^3
S_{wsp}	= end point water saturation after sp.imb	δ	= thickness of pore surface area
S_{orw}	= end point water saturation after forced imb	γ	= gyromagnetic ratio, Mhz/T
S	= pore surface area, m^2		
S/V	= pore surface area to volume ratio, m^{-1}		

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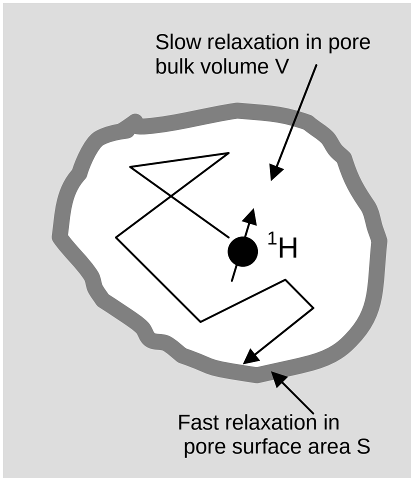

Figure 1. A pore divided into bulk volume *V* and pore surface *S*.

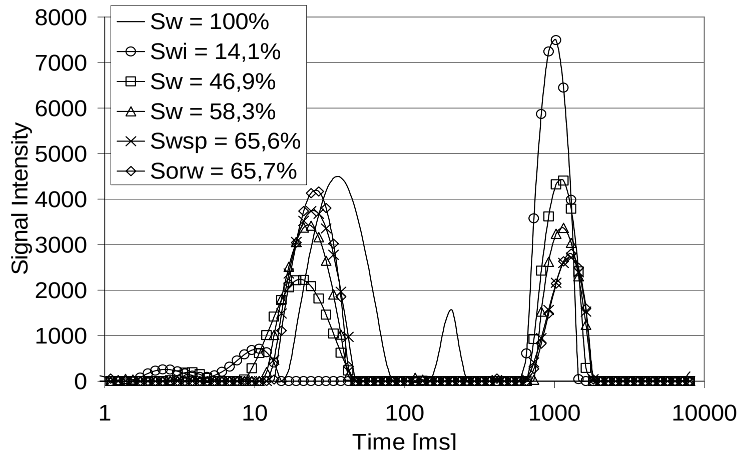

Figure 2. T_2 relaxation time distributions for the Core Plug CP7, I_w= 1.00.

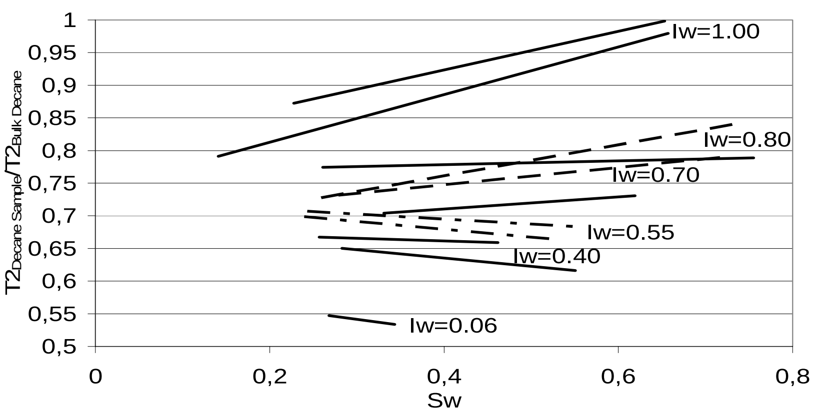

Figure 3. Relative shifts for T_2 for the oil phase (decane) during spontaneous imbibition; as a function of water saturation S_w.

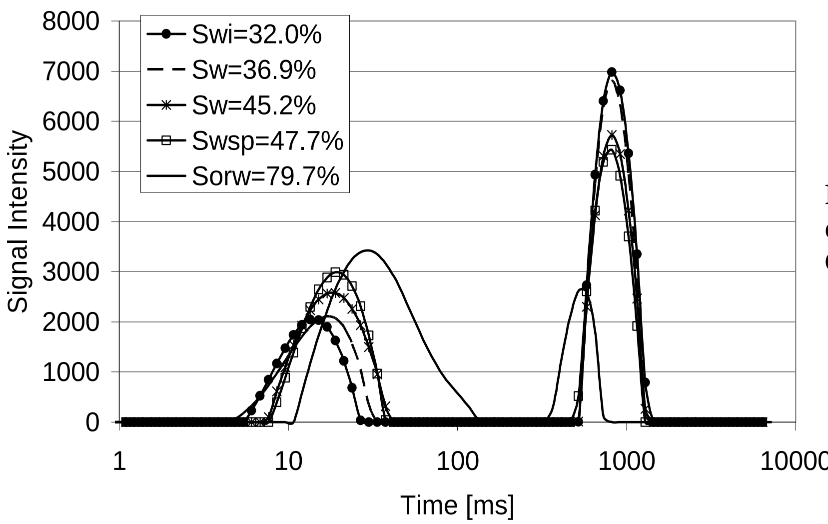

Figure 4. T_2 relaxation time distributions for the Core Plug CP5, I_w= 0.33.

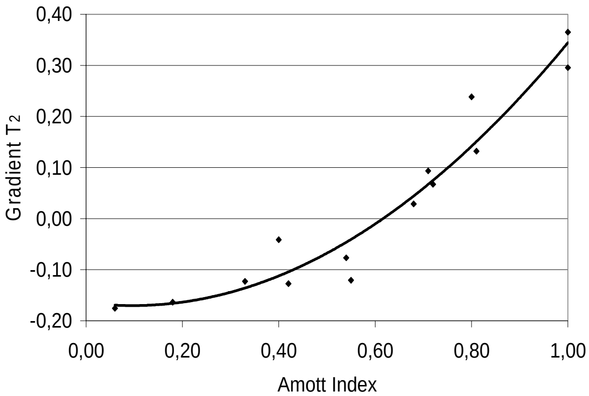

Figure 5. The gradients for the trend lines of relative shifts in T_2 for the oil phase during spontaneous imbibition; as a function of Amott Index.

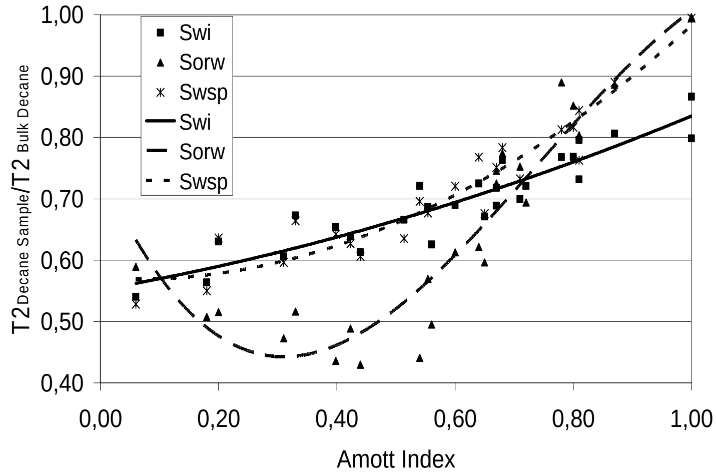

Figure 6. Relative T_2 shifts for the oil phase at S_{wi}, S_{wsp} and S_{orw}; as a function of Amott Index.

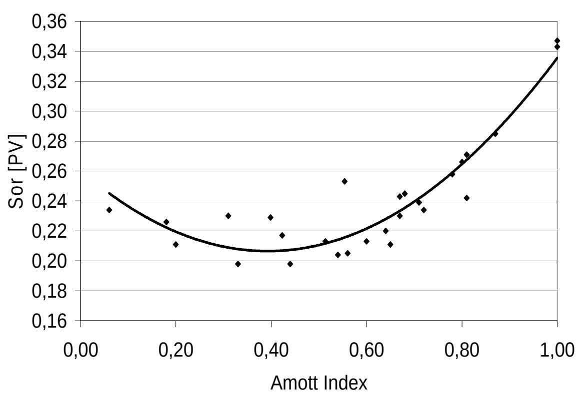

Figure 7. Residual oil saturation as a function of Amott Index.

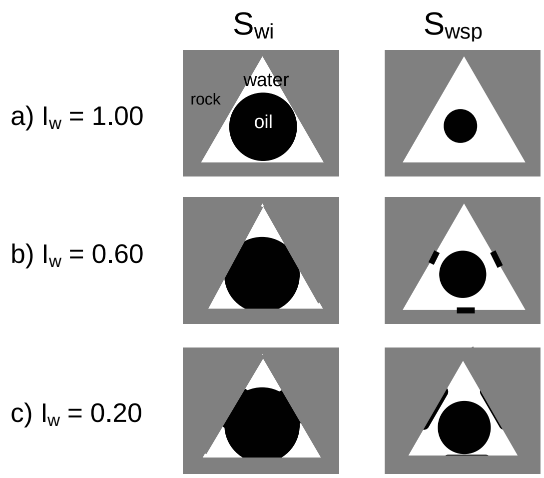

Figure 8. Schematics of a single pore at two different fluid saturations; S_{wi} and S_{wsp}, and at three different wettabilities; strongly water-wet, moderately water-wet and weakly water-wet.