WETTABILITY ALTERATION DURING AGING: THE APPLICATION OF NMR TO MONITOR FLUID REDISTRIBUTION

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ABSTRACT

The changes occurring during aging of reservoir core samples in crude oil, which aims to restore the reservoir wettability, are complex. The dynamic mechanisms involved are still not entirely clear. Understanding the dynamics of wettability restoration in the laboratory will improve our ability to reproduce reservoir conditions before performing core tests and help to ensure that laboratory data are representative of the reservoir.

This paper investigates the changes of fluid distribution occurring at the pore-scale during wettability restoration using a combination of NMR T_2 relaxation data and electrical impedance measurements. Sandstone core plugs were aged in crude oil at various conditions. One sample was aged at atmospheric pressure and a temperature of 35 to 50° C, for more than 100 days while two other plugs were first aged at ambient conditions for 80 days and then at 85° C and 1.38 MPa for 50 more days. NMR relaxation and electrical measurements were performed on all the plugs at regular time intervals during aging. In addition, the Amott-Harvey wettability index was measured on clean and aged cores.

The T_2 distributions as a function of aging time clearly show changes in oil/water configuration at the pore scale. We infer that this can only be due to wettability changes resulting from interactions between the crude oil and the rock surface. Both NMR data and electrical measurements show that wettability alteration can occur before the 40 days traditionally used in the majority of studies, even at room temperature and pressure. These experiments demonstrate the ability of NMR to identify wettability changes and, under certain conditions, to infer the fluid distributions at pore level.

INTRODUCTION

During special core analysis experiments it is important to establish a wettability condition at the outset that is as close as possible to that originally found in the reservoir.

Wettability is one of the major factors controlling the flow and distribution of fluids in a reservoir [1-3]. In recent years, aging core samples in crude oil has become a widely used method for altering wettability [4, 5]. This method is also applied to outcrop rocks in some research studies. It is widely accepted that the wettability status obtained by aging core samples with connate water saturation in crude oil is more realistic and representative of reservoir conditions, than can be achieved using other chemical treatments.

The aging method entails first saturating a cleaned (and thus water-wet) core plug with brine. The brine is then displaced by crude oil until representative initial water saturation is achieved. During this process it is generally assumed that the smaller pores remain water-filled, whereas the oil invades the remainder of the pore space, leaving thin water films on the pore walls and in crevices. Finally, the core containing crude oil and connate water is left for many weeks at reservoir temperature and pressure. It is at this stage that wettability changes may occur in the oil-invaded pores. However, these changes are dependant upon the stability of the water films, trapped between the rock surface and the oil. The pore walls can only become oil-wet if contacted by oil due to the rupture of these films. In this case the core will have achieved a mixed wettability state. These mechanisms have been discussed in more detail by Buckley *et al.* [6].

The fluid distribution at the pore-level in natural rocks has been studied using either Cryo Scanning Electron Microscopy (Cryo-SEM) or Environmental Scanning Electron microscopy (ESEM) [7-11]. Cryo-SEM provides a means of visualizing oil and water position in individual pores over a broken surface. ESEM on the other hand allows the observation of water condensation-evaporation at low pressure on a grain surface or the changes occurring during displacements on the external surface of a plug, such as imbibition of the wetting fluid. However, neither of these techniques can follow the changes occurring within the pores during aging.

The implications of mixed-wet conditions for two-phase flow properties have been investigated extensively using pore network models [12-16]. However, the input data and assumptions used in these models, such as the spatial wettability and fluid distribution, still remain a matter of conjecture and pore scale experimental data is required to validate them.

NMR relaxation measurements can provide some additional information on the behaviour of the rock/fluid interactions. Numerous researchers have used NMR to analyse solid-fluid interactions and demonstrated that NMR can be a useful tool for determining wettability [17-24]. These studies are based on the observation that the relaxation rates are sensitive, among other things, to the interaction, or lack of it, between a fluid and the surrounding solid pore walls.

The electrical properties of rocks at different frequencies have also been used as a means to estimate rock petrophysical properties such as wettability [25, 26]. This is due to the fact that the electrical behavior of a rock results from both its conductive and dielectric response under a varying AC electrical field. For example, the impedance will be affected by the water saturation and its distribution. Thus, it should be affected by wettability, and a consequence of this effect is the well-known dependence of the resistivity index on wettability. Recently, Moss *et al*. [26] have shown that, for sandstones, wettability has a large effect on the impedance-frequency response and as a result suggested that complex impedance could be used to infer wettability.

In this paper we investigate the dynamics of wettability alteration during the aging of sandstone core plugs in crude oil using a combination of NMR T_2 relaxation data and complex impedance measurements. The NMR measurements were used to study the changes in fluid distribution and wettability at different times during aging at various temperature-pressure conditions whilst the electrical measurements were used to verify the fluid redistribution and water continuity.

EXPERIMENTAL

This investigation used core samples from three outcrop sandstones and two plugs were taken from each outcrop block, resulting in a total of six core samples. The plugs' petrophysical properties are given in Table 1.

Table 1. Sample identification and their petrophysical properties. WI: wettability index to water, OI: wettability index to oil, AHI: Amott-Harvey wettability index.

Sample ID	Klinkenberg Permeability (mD)	Helium Porosity (%)	NMR Porosity (%)	WI	OI	AHI
CLEAN Plugs						
Spr3	7	17.6	16.9	0.75	0.00	0.75
Xla3	17	18.1	18.4	0.89	0.00	0.89
Sta4	38	17.3	17.7	0.88	0.00	0.88
AGED Plugs						
Spr4	7	17.5	16.9	0.05	0.19	-0.13
Xla4	17	18.3	18.4	0.04	0.23	-0.19
Sta4	38	17.3	17.7	0.02	--	--

The samples were first cleaned with methanol using Soxhlet extraction and then dried in a vacuum oven. The dry helium porosity and Klinkenberg gas permeability of each sample were determined prior to the start of the experiments. The plugs were fully saturated with synthetic brine and the NMR porosity determined. Table 2 gives the properties of all the fluids used. Next the samples were desaturated with nitrogen on a porous plate to determine the air-brine capillary pressure. The maximum applied pressure was 100 psi. After the initial water saturation was reached, air was replaced by Multipar H oil by placing the samples under oil and vacuum was applied until all the air was removed. The Amott-Harvey wettability index was measured on one set of clean core plugs.

Table 2. Properties of the fluids used.

Fluids	Density @ 20°C (kg/m^3)	Viscosity@ 20°C (mPa s)	T2 bulk @ 34 °C (s)
5% NaCl+1%KCl	1030	1.08	2. 21
Multipar H oil	760	1.13	0.98
Crude oil	830	4.22	1.38

The Multipar oil was replaced with dead crude oil in three core plugs from the different outcrops. The oil was selected as it has been shown previously to change the wettability of reservoir cores [26]. The samples were then loaded in a steel pressure vessel with lid and aged in crude oil at different pressure/temperature conditions. Sample Sta-4 was aged at atmospheric pressure in an oven at 35 °C for 35 days, then at 50 °C for another 73 days (total 108 days). Samples Spr-4 and Xla-4 were first aged at room temperature and pressure for 80 days then for 50 days at 85 °C and 1.38 MPa. NMR T_2 relaxation time and electrical measurements were performed before and during aging. After aging the samples were then loaded in a Hassler cell and the crude oil replaced by Multipar oil and the Amott-Harvey wettability index measured.

NMR measurements

The T_2 relaxation measurements were performed using a MARAN 2 MHz spectrometer (from Resonance Instruments) at 34 °C and ambient pressure. A CPMG pulse sequence was used to generate the T_2 decay. The parameters used for the measurements were: 100 scans, 8000 echoes and an inter-echo time of 200μs. This inter-echo time was selected to minimise diffusion effects due to internal field gradients [27, 28]. The relaxation time distribution was obtained with the DXP programme from Resonance Instruments. The average value of T_2 distribution (T_{2LM} = log mean of T_2 distribution) was calculated as:

$$T_{2LM} = \exp\left(\frac{\sum_i (Sa_i \ \log T_{2i})}{\sum_i Sa_i} \right), \tag{1}$$

where, T_2 is the relaxation time and *Sa* is the signal amplitude.

Complex impedance measurements

The complex resistivity response at various times during aging was measured using a QuadTech 7600 impedance analyser. Before measuring the complex electrical response the sample was loaded into a Hassler cell and a confining pressure of 2.0 MPa was applied. Impedance (*Z*), resistance (*R*) and phase angle (φ) were measured over the frequency (*f*) range of 10 Hz to 2 MHz. Further details of the measurement and set-up can be found in Al-Mjeni, [29]. The NMR and electrical measurements were taken at the same aging time; e.g., within the same day.

RESULTS AND DISCUSSION

The effect of aging at 35°C and 50°C on T_2 distribution for Sta-4, which was initially strongly water-wet, is shown in Figure 1. It can be seen that there is no T_2 signal taking longer than 200 ms from the clean fully brine-saturated plugs. Thus it is inferred that, at irreducible water saturation and before aging, the peak at ~1000 ms corresponds to the oil as non-wetting phase in the larger pores and signals for $T_2 < 100$ ms correspond to the water in the small pores and crevices.

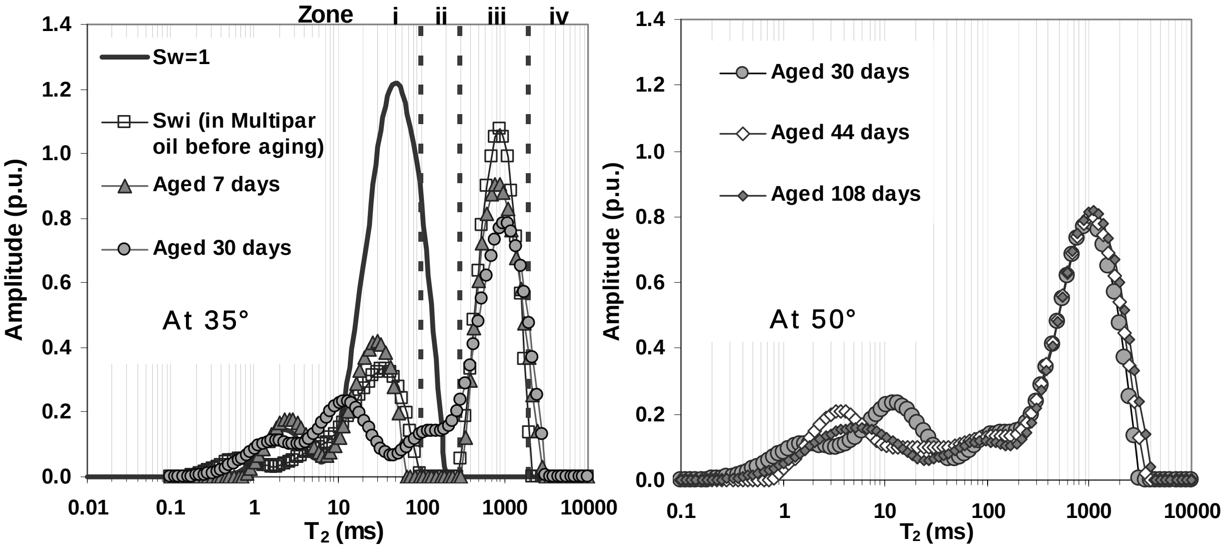


Figure 1. NMR T_2 distributions for Sta-4 as function of aging time.

During the first week of aging at 35 °C significant changes are seen in the T_2 distribution (figure 1a). These can be divided into four zones; i) T_2 values below 100 ms, ii) between 100-300 ms, iii) between 300-2000ms and iv) higher 2000 ms. It is inferred that these changes are due to the oil phase starting to interact with the rock surface. As soon as the aging starts, the water layers and films coating the rock surface begin to reduce their size and the water accumulates in the crevices. This can be inferred from the increase in the T_2 signal below 100 ms (zone i). The collapse of some films allows some oil ganglia to contact the pore surface, which is reflected in a reduction of the amount of oil relaxing as bulk, i.e. the peak at 1000 ms reduces (zone iii). At 30 days there is a reduction in the surface of rock in contact with water, resulting in more water being trapped in crevices with a smaller surface to volume ratio resulting in faster relaxation for these volumes. Also more oil makes contact with the rock surface resulting in a decrease in the bulk oil relaxation and a small peak appearing in zone ii (100-300 ms). The changes in zone iv are due to the fact that some of the water loses its contact with the surface and relaxes at its bulk rate.

After increasing the temperature to 50^{o}C there is a small redistribution of oil and water. The change consists of a small increase in the amount of water (non-wetting) relaxing as bulk (2000-4000ms) and some oil relaxing faster at the rock surface (below 100ms). The amount of oil relaxing as bulk (300-2000 ms) remains unchanged.

Figure 2 shows the electrical response for the same sample. It can be divided into three zones of distinctive frequency dependence. The low-frequency zone corresponds to frequencies below 10KHz in which the response is mainly resistive and may be strongly influenced by electrode polarization. The medium-frequency zone (10–100 kHz) has a relatively flat slope on the impedance vs. frequency plot, and a small phase angle that also changes little with frequency. The high frequency zone (100 kHz–1000 KHz) is distinguishable from the medium one by its higher impedance slope. The transition between the last two frequency zones is characterized by the relaxation frequency of the polarization process [25].

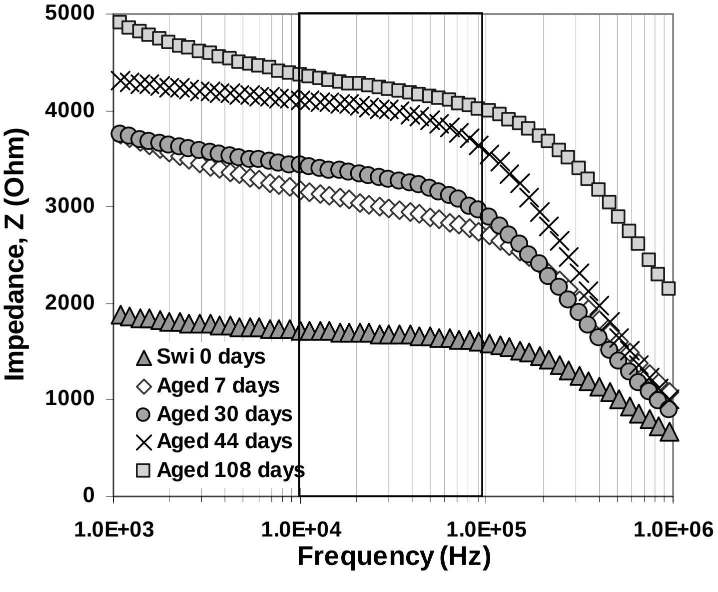
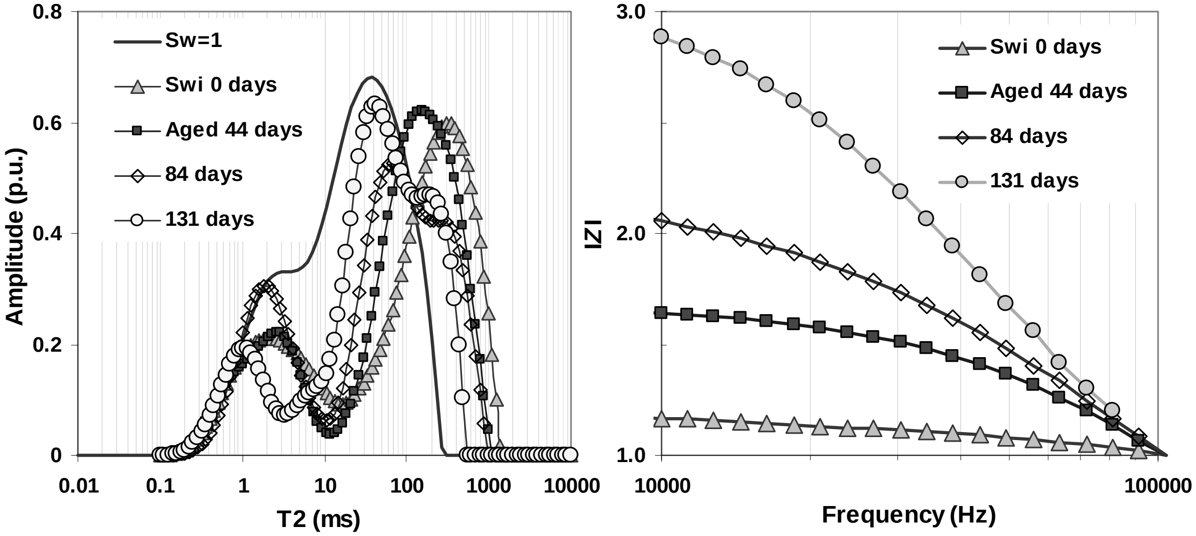


Figure 2. Electrical Impedance, *Z*, against frequency for Sta-4 at different aging times.

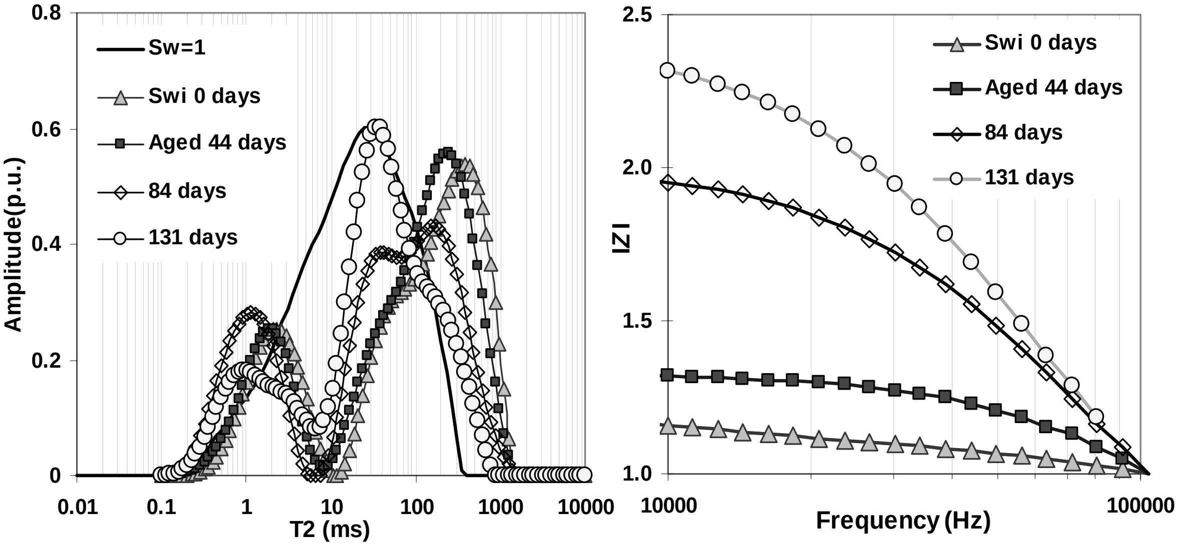
Since the medium-frequency range in figure 2 (10–100 kHz) is fully defined and better characterized, this range was used to monitor the fluid redistribution and wettability changes in the samples. It can be clearly seen that as the aging progresses the electrical impedance increases because the water starts to lose some of its continuity. At the same time the oil phase starts to contact the rock surface. Therefore, the complex impedance observations are consistent with the T_2 measurements. They suggest that there is a gradually change in the fluid distribution during aging as more water becomes discontinuous. It is worth noting that the NMR T_2 distribution provides more information as to where in the pore space these changes occur.



(A) **(B)**

Figure 3. Wettability alteration for Xla-4 as a function aging time at different conditions, A) The NMR T_2 distribution shifts to shorter relaxation as aging time increases and B) The normalized impedance increases over the frequency range as aging proceeds.

Figures 3 and 4 show the T_2 distributions and the normalized complex impedance ($|Z|_f = Z_f / Z_{100\mathrm{KHz}}$) for different aging conditions for samples Xla-4 and Spr-4 respectively. For Xla-4 (Figure 3a), some of the changes observed during aging at room conditions were similar to those described in the previous example. However, no bulk water relaxation was observed during aging. Thus the water still behaves as the wetting fluid even after aging. This is probably due to the presence of clays that remain water-wet, while the oil wets the external clay surfaces and larger clean pores. After aging for 44 days at room conditions, the peak of the distribution has moved from 400 ms to 150 ms, indicating that part of the oil phase has come in contact with rock surface and is relaxing faster. During aging the whole T_2 distribution is shifted to lower relaxation times whilst there is an increase in the NMR signal below 100 ms. Electrical measurements during aging (Figure 3b) support the thesis that fluid redistribution occurs. An increase in impedance with time is consistent with the water phase losing continuity while the increase in slope at intermediate frequencies is consistent with the sample becoming mixed-wet [26].



(A) **(B)**

Figure 4. Wettability alteration for Spr-4 as a function of aging time at different conditions, A) The NMR T_2 distribution shifts to shorter relaxation times as aging time increases and B) The normalized impedance increases over the frequency range as aging proceeds.

The NMR and impedance response for Spr-4 during the aging process is very similar to Xla-4 as can be observed by comparing Fig. 4 and Fig. 3. The effects are more evident in Fig 4-A when comparing the T_2 distributions before and after aging. After aging the largest peak decreases and shifts toward shorter times, the signal at intermediate values of T_2 (10 to 100 ms) increases, and the signal at small values of T_2 (1 to 10 ms) decreases. The decrease in signal between 1 and 10 ms may be due to more water being trapped in crevices with a large surface area to volume ratio. The overall shift of the core aged T_2 distribution towards the water-saturated distribution indicates that water and most of the oil are in contact with the rock surface and relaxing via contact with the surface.

Wettability indices

Wettability can be quantified during restoration by using the NMR wettability index proposed and validated by Al-Mahrooqi *et al.*[23] Their index is defined as:

$$WI_{NMR} = \left(\frac{T_{2LM,Swi} - T_{2LM,Sor}}{T_{2LM,Sor}} \right) \tag{2}$$

Figure 5 shows the changes in the wettability index during aging of samples Spr-4 and Xla-4. For both samples, the wettability alteration begins immediately. During the aging at ambient conditions there is a steady decrease in wettability from strongly water-wet to weak mix-wet. When the temperature and pressure were raised to 80°C and 1.38 MPa, there is an increase in the rate of wettability alteration as seen by a larger shift in wettability index to negative values. The NMR wettability indices, before and after aging, have a good correlation with the Amott-Harvey index, which was measured for clean and aged samples (Table 1). Thus the NMR index provides a quantitative method for determining the wettability alteration occurring during aging with crude oil.

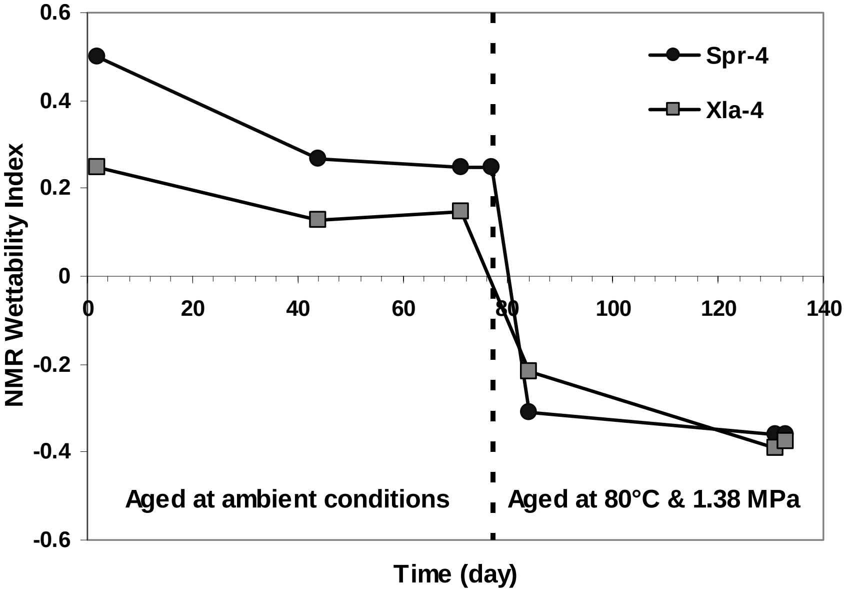


Figure 6. NMR wettability index as a function of aging time for samples Spr-4 and Xla-4.

CONCLUSIONS

The changes in NMR T_2 distributions and electrical impedance were monitored during the aging of clean sandstone plugs in crude oil. The main conclusions from these experiments are:

- The small changes in NMR T_2 at short times during aging are consistent with the smaller pores being always filled with water throughout aging. On the other hand, there is a significant variation in the signal at larger relaxation times, which indicates the wettability alteration of the large pores.
- During the aging period the signal due to bulk oil relaxation reduces whilst the signal at shorter times increases. Again this is consistent with some of the initially non-wetting oil contacting the rock surface.

- Electrical impedance measurements at frequencies 10 kHz to 100 kHz confirmed that there is a gradual change in the fluid distribution during aging in crude oil. There is an increase in the electrical impedance and change in its frequency dependence as the aging time increases.
- Wettability alteration begins at the start of aging and occurs more rapidly at higher temperatures.
- The wettability index based upon log mean T_2 measurements indicates on overall change in the cores' wettability from water-wet to mixed-wet. This change seems to be strongly dependant on temperature.

Overall the changes in NMR T_2 distribution and electrical impedance measurements are consistent with existing models of how mixed wettability develops during aging and during initial reservoir filling with oil. They should provide a useful addition to the petrophysical toolset to enable the monitoring of wettability changes during aging to optimise the time spent aging cores and assess how the rock/fluid system approaches equilibrium.

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