

CARBONATE NMR MEASUREMENTS IN A COMBINED AMOTT-USBM WETTABILITY METHOD

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ABSTRACT

NMR measurements were performed along with the stages of a combined Amott-USBM method for some Brazilian deep-water carbonates. Guided by the T_2 signature of non-confined brine and dead crude oil, monophasic and biphasic T_2 distributions were interpreted revealing pore occupancy and wettability of micro and meso-to-macro pores. Consistent T_2 shifts were observed after core aging, imbibition and second drainage. The results indicate that simple 1D-NMR shall support standard methods that cannot resolve saturation and wettability per porosity type.

INTRODUCTION

Shortly after NMR phenomenon discovery in the late forties, the enhancement of relaxation time rates for the wetting phase was noticed [1]. Since then, many studies have been performed on NMR wettability based either on modeling or experimental approaches [2-4]. Although most of these works introduce NMR indices and compare them to the industry standard indices, they do not necessarily must have the same response because these techniques rely on different physical grounds. Instead, for improving conventional methods response, this work evaluates transverse relaxation times (T_2) in the different saturation and wettability conditions availed from the stages of a combined Amott-USBM method [5,6]. As indicated in Figure 1a, T_2 measurements were acquired after 1) total water saturation ($S_w=100\%$), 2) first drainage with dead crude oil up to irreducible water saturation (S_{wi}), 3) three-months aging in the crude oil, 4) spontaneous plus forced water imbibition up to residual oil saturation (S_{or}) and, 5) spontaneous plus forced drainage with crude oil up to final water saturation (S_{wf}).

As indicated in Figure 1b, the water Amott index (I_w) measures the displacement-by-water ratio, which is the oil volume displaced by spontaneous water imbibition (ΔS_{ws}), relative to the total oil volume displaced by spontaneous and forced water imbibition ($1-S_{wi}-S_{or}$). The oil index (I_o) is analogously defined and the difference between water and oil indices is known as the Amott-Harvey index (I_{AH}) which is bound by $-1 < I_{AH} < +1$, Figure 1b. In contrast, the US Bureau of Mines (USBM) index is calculated with the areas under the capillary pressure curves that describes displacement of oil by water A_i (forced imbibition) and the displacement of water by oil A_d (second forced drainage), Figure 1c.

For example, a carbonate with index -1 would require 10 times more energy for imbibition than for drainage (and vice versa for index +1). Although the USBM index is more sensible to neutral wettability, it cannot differ between neutral (I_w and I_o are equal and low) and mix (I_w and I_o are equal and high) wettability.

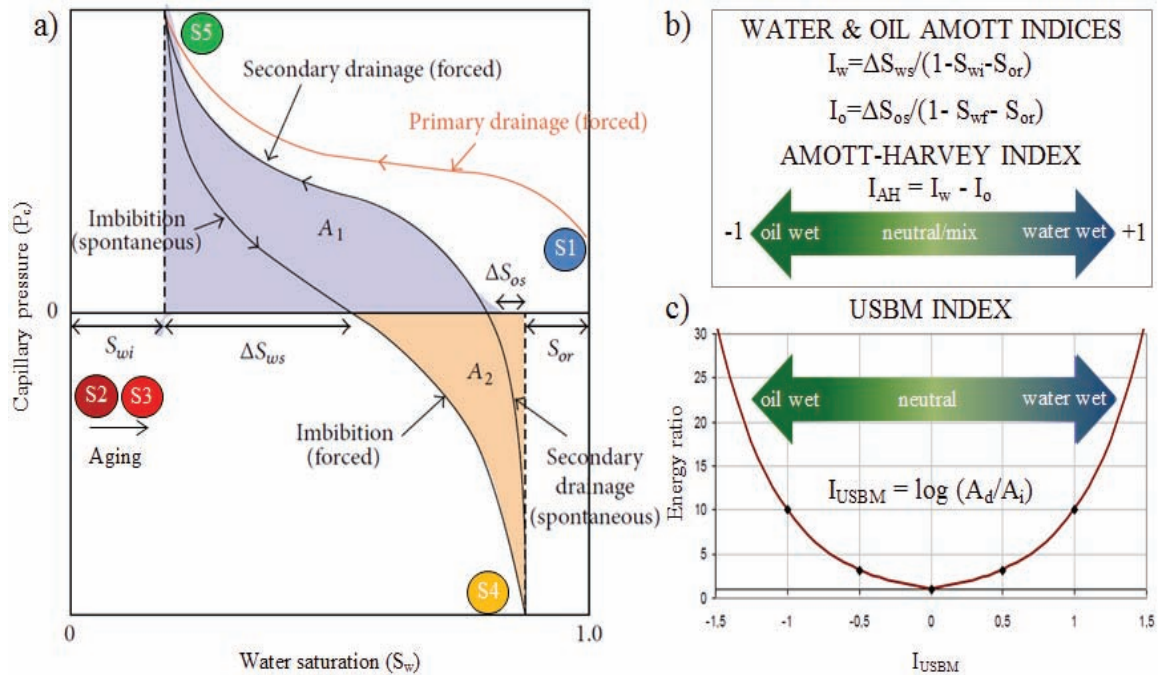


Figure 1: a) Complete cycle of the Amott-USBM method showing the five stages where T_2 measurements were acquired. The classical wettability indices are also defined: a) Amott-Harvey and c) USBM.

EXPERIMENTAL

X-ray microtomography (μ CT) and routine core analyses (RCAL) were used for selection of seven representative core plugs from a Brazilian Pre-Salt carbonate reservoir. Special core analyses (SCAL) were performed at the reservoir temperature of 60 °C. Brine salinity in NaCl equivalent was 182 g/l; brine density and viscosity was 1.09 g/cm³ and 0.65 cP, respectively, and dead crude oil density and viscosity was 0.86 g/cm³ and 11.23 cP, respectively. Spontaneous imbibition and drainage volumes were acquired until production stabilization, between 25 and 75 days. Without confinement, forced imbibition and drainage were performed with a centrifuge in 15 increasing capillary pressure steps up to 100 psi (at the face of the core plug). The Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence were used for measuring T_2 in a 2.2 Mhz (for ¹H) benchtop NMR analyzer (Maran DRX-HF, Oxford instruments, UK). A full polarization time and a minimum signal to noise ratio of 100:1 were used. T_2 distributions were inverted in the WinDXP program (the Maran accompanying software) using 256 bins which were then normalized to a unitary sum of amplitudes. Further details on NMR phenomenon, data acquisition and inversion can be found in the reference [7].

RESULTS AND DISCUSSION

Bulk transverse relaxation time T_{2b} of the brine and the crude oil are shown in Figure 2a (non-confined in the rock). In brine, ^1H is present only in the molecules of water and thus T_{2bw} distribution is quite narrow. In contrast, dead crude oil presents a very broad T_{2bo} distribution due to the diversity of hydrocarbon molecules (between tens and hundreds of thousands) that contains ^1H . Long T_{2bo} is related to light components (e.g. paraffins and aromatics) holding small molecules with high mobility. Short T_{2bo} is associated to heavy components (e.g. resins and asphaltenes) holding big molecules with low mobility. However, if water and oil are confined in a porous media, relaxation time rates are enhanced due to the interaction with pore surface. Considering a fast diffusion regime and assuming no diffusional relaxation effects due to magnetic field gradients nor diffusion pore coupling [7], T_2 of water and oil confined in a pore can be described as follows [3]:

$$\frac{1}{T_2} = \frac{1}{T_{2bw}} + \rho_w \frac{A_w}{S_w V_p} + \frac{1}{T_{2bo}} + \rho_o \frac{A_o}{S_o V_p}, \quad (1)$$

Where ρ_w and ρ_o are the T_2 surface relaxivity for water and oil, respectively; V_p is the pore volume; S_w and S_o are the fractional water and oil pore saturation ($S_w + S_o = 1$), respectively and; A_w and A_o are the fractional water and oil pore surface area ($A_w + A_o = A$), respectively. From equation 1, the characteristic length (R) of a spherical pore site ($R/3 = V/A$) occupied by a fluid which has a single T_{2b} is $R(T_2) = 3\rho(T_2 T_{2b}/T_{2b} - T_2)$. Figure 2b plots $R(T_2)$ for brine and each of the three crude oil components with $\rho_w = 0.006 \mu\text{m}/\text{ms}$ (average values based on mercury-injection data comparison) and assuming $\rho_o = \rho_w/3$ as in reference [8]. Characteristic lengths of 1 and 10 μm were considered as thresholds among micro, meso and macro pore types.

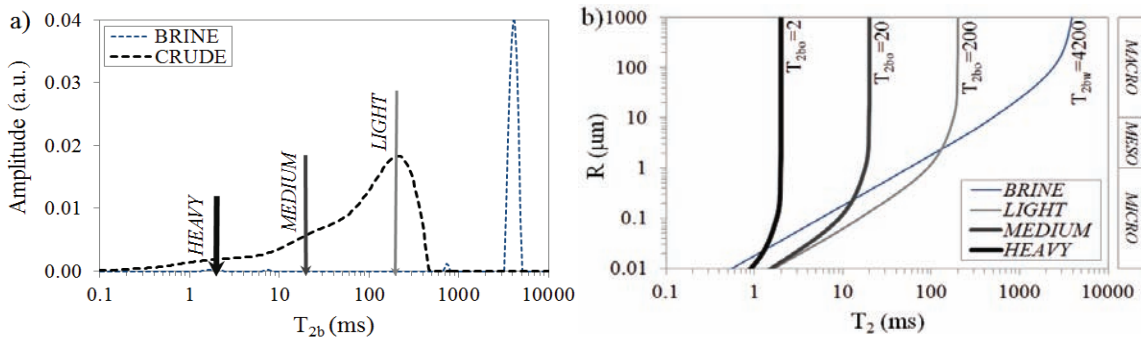


Figure 2: a) Bulk T_2 for brine (T_{2bw}) and crude oil (T_{2bo}). b) Characteristic length (R) of spherical pore sites as a function of monophasic T_2 for brine and crude (although the oil components cannot be separated, their relaxation behavior is illustrated separately, as if they were three different oils).

The studied carbonates are high quality reservoir facies with good porosities (15-20 %) and permeabilities (8-1552 mD) responding with long monophasic (brine) T_2 distributions, Figure 3a. Higher T_2 are associated with higher permeabilities which is explained by the bigger characteristic lengths (brine curve of Figure 2b). When these

carbonates were desaturated by crude oil (S_{wi} ranging from 13 to 25 %), previous T_2 -based differences in pore structure became less evident and all biphasic T_2 distribution reduce to a similar shape of the crude oil bulk response, black dotted curve in Figure 3b. This indicates that crude is in meso-to-macro pores relaxing almost like T_{2bo} distribution (Figure 2b shows that surface relaxation is low in such pore types even for light oil components). After brine imbibition (S_{or} ranging from 3 to 29 %), some previous features of macropores (300 to 3000 ms in Figure 3a) are clearly recovered in Figure 3c between 600 and 4000 ms. The observed shift towards T_{2bw} indicates a decrease of the brine surface relaxation component (less contact with the pore walls) compared to the bulk relaxation component (Equation 1). Although residual oil occupies smaller sites after brine imbibition, characteristic lengths of these sites would be in the same order of magnitude (lets say, for instance, a quarter of the meso-to-macro pore sizes). Imbibed brine may also reduce contact with pore walls further explaining why it still relaxes as T_{2bo} distribution (which is summed with the irreducible brine signal from micro pores, $T_2 < 500$ ms). Imbibed brine is not totally driven out after second drainage ($S_{wf} - S_{wi} > 0$) and its portion more isolated from the pore walls, responding in the T_2 range of 600 to 2000 ms (Figure 3d), prevents hysteresis back to the distribution shapes of Figure 3b.

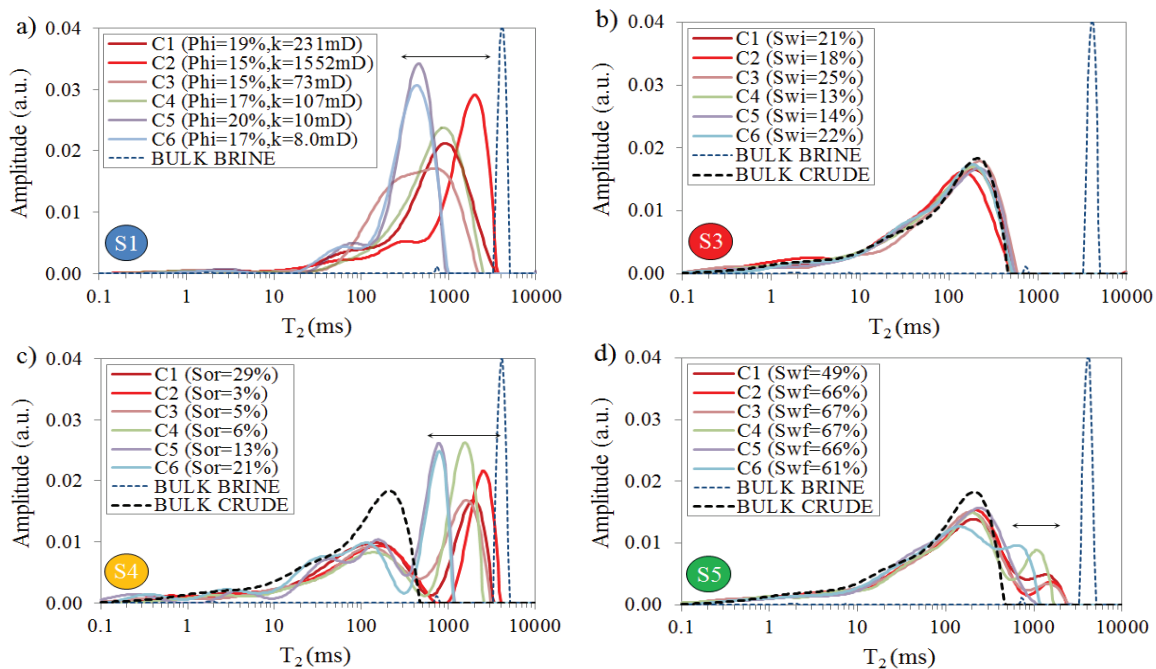


Figure 3: T_2 distributions for the carbonate plugs (continuous curves) after: a) fully water saturation, b) drainage up to S_{wi} and aged, c) imbibition up to S_{or} and d) drainage up to S_{wf} . T_{2b} distribution of non-confined brine and crude oil are also shown as reference (black and blue dotted curves, respectively).

The curves for the three first stages are plotted together for samples C4 and C5 in Figure 4a and 4b, respectively. Strictly, the standard wettability methods started only after native wettability restoration, which was performed by aging the samples in crude oil for three months. The bigger shift to short T_2 agrees with the more oil-wet conditions indicated by

the Amott and USBM methods of sample C4. After aging, the surface wetted by crude oil in meso-to-macro pores (A_o) increases and so does T_2 rates (Equation 1). The four stages presented in Figure 3 are plotted all together in Figure 5. Partial exchange between oil and water is highlighted in black shading for sample C4 after imbibition (Figure 5a) whereas the opposite exchange is highlighted in blue shading for sample C5 after second drainage (Figure 5b). The biphasic distributions of Figure 5 are shown in Figure 6 subtracted by the oil signal which was considered to have the same shape of T_{2bo} distribution (sum of amplitudes normalized to $1-S_{wi}$, S_{or} and $1-S_{wf}$ for stages 3, 4 and 5, respectively). According to the classical cutoff interpretation, calculated with the S_{wi} value on the monophasic T_2 distribution, irreducible brine is in micro pores and free brine is in meso-to-macro pores. While subtracted irreducible brine in stage 3 is within the monophasic T_2 distribution agreeing especially for shorter T_2 , its apparent increase in the stage 4 and 5 is probably brine coating the walls of meso-to-macro pores or occupying reduced sites in such pore types. In contrast, free brine in pore sites with less contact with the pore walls can have longer T_2 than the monophasic response which is due to a decrease of surface relaxation and consequent bigger influence of bulk brine components.

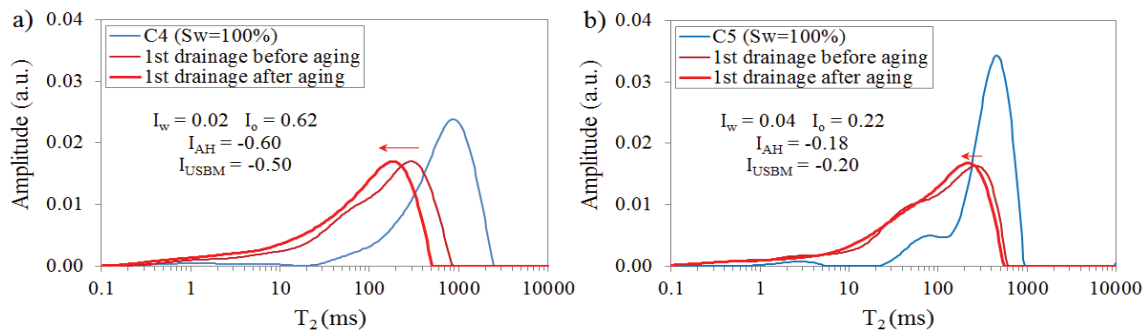


Figure 4: Monophasic (S1) and biphasic (S2 and 3) T_2 distribution for carbonates plugs a) C4 and b) C5.

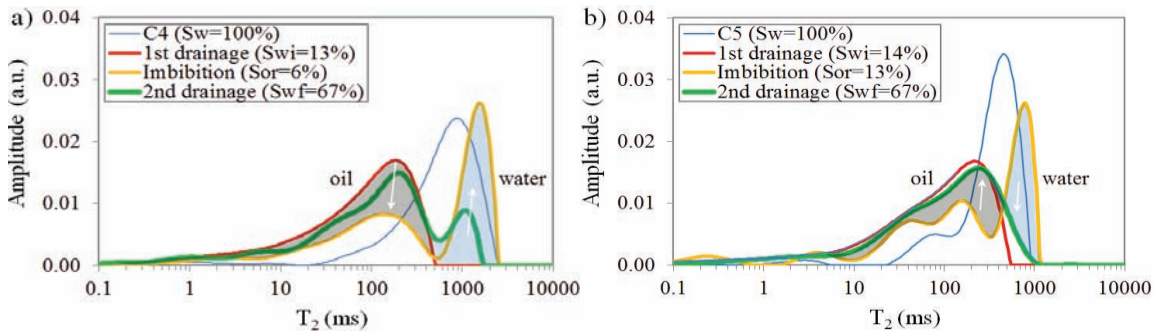


Figure 5: Monophasic (S1) and biphasic (S3,4 and 5) T_2 distribution for a) C4 and b) C5.

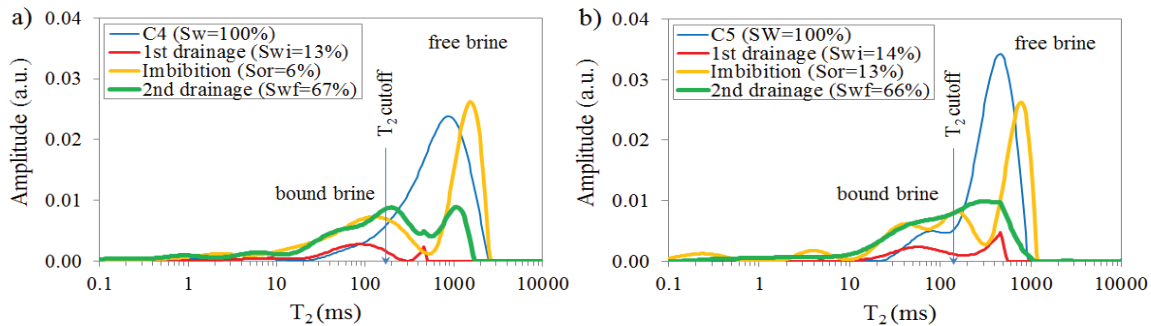


Figure 6: Monophasic (S1) and brine signal of biphasic (S3,4 and 5) T_2 distribution for a) C4 and b) C5.

CONCLUSION AND PERSPECTIVES

NMR transverse relaxation times (T_2) were interpreted for some Brazilian deep-water carbonates under the different saturation and wettability conditions of a combined Amott-USBM method. While monophasic T_2 distribution was more sensible to the samples variation in characteristic pore lengths, the biphasic T_2 distributions had signals overlapped from the fully-brine-saturated micro pores (thus water-wet) and the brine and crude oil presence in meso-to-macro pores. Several arguments were presented showing that the crude oil relax quite close to its bulk T_2 signature which allowed a simple signal separation in T_2 -domain. Samples with the Amott-USBM indices indicating a preferably oil-wet condition presented T_2 distributions shifted to shorter values after restoring native wettability. With the aging, crude oil increased its contact with the surface of the meso-to-macro pores. After imbibition and second drainage, the presence of residual crude oil makes brine relax in different sites with more or less contact with the pore walls (i.e. shorter or longer T_2 , respectively). This work is been extended for different carbonate reservoirs with a bigger number of samples. The evaluation shall be improved with others NMR techniques such as spatial T_2 and diffusion- T_2 measurements.

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