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Chemical Resolution in T_2-T_1 correlations

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Abstract

Oil and water fractions have been identified in fluid saturated carbonate rock cores using a novel T_2-T_1-δ pulse sequence. The inclusion of the chemical shift dimension δ allows T_2-T_1 plots to be generated independently for the oil and water. The T_2-T_1-δ pulse sequence utilises a “double-shot” T_1 measurement that provides free induction decays (FIDs) as a function of both relaxation times for suitably broad line samples. The T_2-T_1-δ data set is acquired in the same experimental time as a conventional T_1-T_2 measurement (without chemical resolution) of equivalent data density. Here we demonstrate that different behaviour can be observed between the oil and water fractions in water wet and preferentially oil wet cores, and that saturation states can be determined. This technique could provide a quantitative NMR measure of wettability.

Keywords

Relaxation correlations; Laplace inversion; chemical shift; permeable rocks; wettability.

1. Introduction

T_1-T_2 correlations are useful for determining the T_1/T_2 ratio as a characteristic parameter of permeable rocks [1]. However, the presence of both oil and water can complicate the analysis. Sedimentary rocks are therefore analyzed commonly with D-T_2 correlations at low magnetic fields utilising the distinct difference in diffusion coefficient D of the two liquids [2], although it is still possible to observe overlap of the two components. Recently we have presented a novel T_2-T_1-δ correlation [3] where the chemical shift dimension δ allows the water and oil fractions to be identified unambiguously. This method could lead to a quantitative measure of the wettability of the pore surfaces within the core since T_1/T_2 is related to the strength of interaction at the liquid-solid interface [4]. Previous NMR wettability measurements have focused on low-field T_2 relaxometry. Looyestijn and Hofman demonstrated a forward model for separating the overlapping T_2 response from oil and water, both of which are subject to the pore size distribution in the sample [5], and applied this to NMR well logs [6]. Such an approach requires some *a priori* knowledge or assumptions about the rock in order to extract a wettability index. The method we propose has no such analytical limitations, although it can only be applied as a laboratory measurement at the present time.

2. Methods and Materials

The T_2-T_1-δ pulse sequence [3] comprises a CPMG echo train [7] followed by the "double-shot" T_1 measurement [8,9]. The "double-shot" T_1 pulse sequence requires the spin ensemble to be stored on the $\pm z$ axis in successive scans. This is achieved by phase cycling of a 90^o storage pulse placed at the end of the CPMG echo train. The T_1 measurement is obtained from a series of small tip angle α pulses that drive the spin ensemble to some arbitrary equilibrium level in a single scan. The up/down store cancels out this factor leaving an exponential decay with a time constant T_1. After each α pulse, a FID with 512 points (dwell of 10 µs) was acquired and Fourier Transformed to provide the chemical shift information. In the first (T_2) dimension, 32 data points were acquired at echo times of t_E = 2 ms to 2 s. In the second (T_1) dimension, 128 data points were acquired at intervals of ~ 60 ms, spanning recovery times of 1 ms to 8 s. Each T_2-T_1-δ data set was acquired in 1 h. The T_2-T_1 data were inverted using a 2D Fast Laplace Inversion [1].

The rocks studied were all Portland carbonate cores. Scanning Electron Microscope (SEM) images, Fig. 1, revealed consistent crystal structures at every length scale. Mercury intrusion porosimetry measurements (not shown) indicated a bimodal pore throat size distribution. The rock surface is water wet initially. Some cores were saturated with a silane treatment to provide uniform oil wet pores. The water wet rocks were initially saturated with deionised water. The NMR responses of the initial saturated samples were indistinguishable. Different volumes of dodecane were pumped through the cores corresponding to 1/3, 2/3, and 2 Pore Volumes (PV, where 1 PV ≈ 14.5 cm^3). T_2-T_1-δ data sets were recorded for each core. The same process was applied to the oil wet cores except they were initially saturated with dodecane which was then displaced with water. All the cores were stored under the non-wetting fluid between measurements.

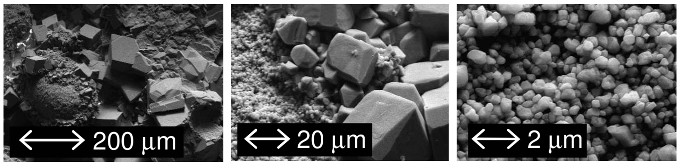

Fig. 1: SEM images of Portland carbonate recorded at 3 different length scales. The same calcium carbonate crystal shapes are present at each length scale.

3. Results and Discussion

Example T_2-T_1-δ correlations are shown in Fig. 2 for (a,b) water wet and (c,d) oil wet carbonate cores. The insets shown the chemical shift spectra with the water (blue) and oil (red) peaks highlighted as appropriate. In the water wet core the water signal, Fig. 2(a), lies on the line $T_1 = 8T_2$ (blue dashed diagonal), indicating the water is in contact with the pore surfaces. The oil signal, Fig. 2(b), lies close to the $T_1 = T_2$ line, indicating the oil does not experience the surface. In the oil wet core the water signal, Fig. 2(c), lacks the short relaxation time component seen in (a), suggesting there is less interaction with the surface. There still appears to be some enhanced surface relaxation, likely due to incomplete surface treatment. An additional oil peak, Fig. 2(d), is present in the T_2 dimension (the centre denoted by the vertical black line) indicating the oil is in contact with the pore walls. However, the single T_1 component suggests the surface interaction is different compared to water.

Fig. 3 shows the relative volumes of oil and water in the cores determined from the NMR data and volumetric analysis of the displaced liquids for the (a) water wet and (b) oil wet carbonates. In the water wet rock there is good agreement between the NMR and volumetric measurements: an irreducible water saturation of ~ 0.5 PV was observed. However, in the oil wet rock, there was a significant difference in the fluid volumes. This discrepancy has been attributed to additional water ingress whilst the cores were stored under water as a result of the surface treatment degrading. An irreducible oil saturation of ~ 0.4 PV was observed.

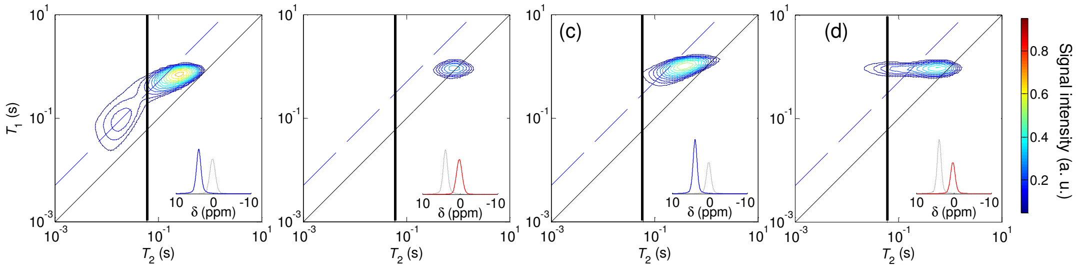

Fig. 2: T_2-T_1-δ correlations plots for (a,b) water wet and (c,d) oil wet carbonate cores saturated with a mixture of water and dodecane. The chemical shift dimension allow the (a,c) water and (b,d) oil signals to be distinguished in each case. The inserts show the spectral peaks for the water (blue) and oil (red) referenced to $CH_3 \equiv 1.27$ ppm.

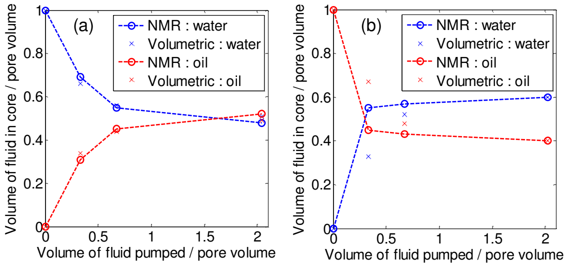

Fig. 3: Volumes of oil and water in the (a) water wet and (b) oil wet carbonate cores determined by volumetric measurement of the displaced liquids and analysis of the NMR T_2-T_1 correlation plots.

3. Conclusions

In this paper we have suggested the application of a novel three-dimensional T_2-T_1-δ correlation measurement to the study of reservoir rock cores saturated with a mixture of oil and water. The inclusion of the chemical shift information allows T_2-T_1 plots to be extracted independently for the oil and water signals. Different behaviour was observed for the two liquids in water wet and oil wet cores. Whilst this technique is limited to the laboratory, the possibility of providing a quantitative NMR wettability index could make the T_2-T_1-δ correlation an important tool for petroleum engineers in the future.

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