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WETTABILITY AND FLUID SATURATIONS DETERMINED FROM NMR T_1 DISTRIBUTIONS

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The abundance and distribution of brine and decane are determined from T_1 distributions at different stages of a water-flood test in water-wet and oil-wet chalks. The T_1 distributions generated from multi-exponential decomposition of inversion-recovery data provide more information than obtained from stretched and bi-exponential fits. Chalk samples because of their uniform pore size and ideal sedimentary rocks for NMR investigations of wettability since water and decane interactions with pore walls of differing wettability are easily distinguished.

Keywords: **Multicomponent relaxation; Wettability; Fluid saturations.**

INTRODUCTION

The surface sensitive nature of proton NMR relaxation measurements makes it an ideal probe to determine changes in wettability of porous media altered by the adsorption of hydrophobic agents on the pore walls. Glass bead packs saturated with water and treated with organic films to make the sample predominantly oil-wet illustrated that longitudinal relaxation times T_1 are greater for oil-wet samples than for water-wet.[1,2] Measurements on sandstones[3] and carbonate[4] whose wettability was altered by different cleaning methods also had greater T_1 values associated with the oil-wet samples. These studies[3,4] also reported results for samples saturated with both oil and water. The present study shows how the transformation of data into a distribution of relaxation times clearly indicates the distribution of fluid phases in the pore space in samples of varying wettability. This study focuses on fluid distributions and saturations at various stages of a water flood test in both water-wet and oil-wet chalks.

SAMPLES AND METHODS

Chalk samples were used in these experiments because of their small and highly uniform pore size. Samples include those from outcrop (#s 1, 2) and those from a subsurface reservoir (#s 20, 25). Each sample was divided into two equal plugs, as characterized by similar porosity and permeability (Table 1). Median pore throat size was determined by conventional mercury injection porosimetry methods where intrusion pressures were converted into pore throat widths. The first set of samples (A) were untreated before measurement. These samples are naturally highly water-wet, except for 25, which is intermediate water-wet. The second set of chalks (B) was altered to an oil-wet state by flowing 10 pore volumes of an oil-based drilling mud through the plug and aging for several days. Wettability of these chalks was determined by standard Amott tests as the ratio of spontaneous to forced displacement of fluid where 1.0 is strongly water-wet, −1.0 is strongly oil-wet, and 0.0 is neutral[4] (Table 1).

Table 1. Standard properties of chalk samples

Sample	Porosity	Permeability (md)	S_{wi}	Wettability index
1A	32.71	2.42	13.2	0.769
2A	33.44	2.37	9.8	0.817
20A	34.07	2.70	12.9	0.208
25A	31.87	0.93	16.5	0.712
1B	31.74	2.29	4.07	−0.604
2B	31.72	2.14	3.7	−0.709
20B	34.90	3.10	11.0	−0.876
25B	33.37	1.09	6.2	−0.752

Inversion-recovery measurements on 1 inch diameter plugs were made using 30 recovery times between 0.1 ms and 13 s on a commercially available 10 MHz benchtop spectrometer. Data were analyzed with stretched exponential,[5] bi-exponential, and multi-exponential fits.[6,7] The advantage offered by the multi-exponential fits is the *a priori* assignment of T_1 values that cover the range of interest with a large number (30 in this study) of terms. The solution of a seemingly ill-posed problem was achieved with robustness by the inclusion of a regularization term into the fitting cost function that is minimized by a nonlinear least squares algorithm.[7]

RESULTS

These water-wet chalk samples when fully saturated with water are characterized by a narrow distribution of T_1's, between 45 and 80 ms. Pore throat radii range between 0.27 and 0.60 microns. Surface relaxivity is calculated with these estimates of throat dimensions, and the stretched exponential T_1 value. Surface relaxivities of 1.0 to $4.0 * 10^{-4}$ cm s^{-1} are comparable to values for highly water-wet porcelain samples[8] and other carbonates, and are an order of magnitude less than the average surface relaxivity for sandstone.[6] Comparison of surface relaxivities among studies is strongly dependent upon the method used to independently determine pore dimensions. Water-wet chalks saturated with decane have relaxation time distributions centered between 250 and 650 ms (Table 2). Surface relaxivities for the decane-saturated chalks are a factor of 4 to 5 less than the water-saturated samples.

The treated oil-wet chalks when fully saturated with water also have a narrow distribution of T_1's, with mean values comparable to the water-wet samples. This is contrary to expectations based on simple physical models of relaxation enhancement, which would predict that oil-wet pores saturated with water should have longer T_1's than water-wet pores. Incomplete core cleaning of water-saturated chalks was responsible for similar T_1 values for water- and oil-wet chalks in a previous study.[4] In this study the oil-based drilling mud treatment for these chalks introduces paramagnetic ions that counteract the reduced surface interactions created by an oil-wet pore wall. The competing relaxation mechanisms of paramagnetics and pore wall wettability limit any quantitative interpretation of relaxation. Nonetheless, there are qualitative aspects of the NMR relaxation that are unique to these highly oil-wet samples.

The initial step in the water flood test is the displacement of the moveable water by decane, which produces a sample with roughly 10% water remaining in the smallest pores and as films coating pores. This remaining water is termed S_{wi}, the irreducible water saturation. All of the water-wet chalk samples have a bimodal T_1 distribution at this stage (Fig. 1). The two outcrop samples have a small mode at 10 ms that corresponds to S_{wi}. This mode is shifted towards shorter times from the 100% brine-saturated T_1 distribution. The second mode for these samples is at 1400 ms which corresponds to the relaxation time for bulk decane. The short relaxation time mode for the two water-wet reservoir samples, 20 and 25, is closer to the relaxation time of 50 ms for 100% saturated. The longer mode at 1000 ms is shifted towards shorter times from the bulk decane relaxation.

NMR estimates of S_{wi} compare favorably with water saturations determined by conventional core measurements (Fig. 2). Water and decane saturations are estimated from the peak areas of the two relaxation time modes and normalized. The peak areas that are associated primarily with decane and water are corrected for the slightly different proton densities (hydrogen abundance/unit volume) of brine and decane. One advantage to the NMR method is that the measurement is not affected by small weight losses that accompany any core handling.

Spontaneous imbibition of water forces out some of the decane during the next stage of the water flood. The relaxation mode intensities change for the T_1 distribu-

Table 2. Comparison of relaxation times (ms) of water-wet and oil-wet sample 2 at different saturation conditions with stretched and bi-exponential fits

State	T_1	α	T_{1S}	A_S	T_{1L}	A_L
Water-wet						
100% Water	43.3	0.932				
100% Decane	613.9	0.950				
S_{wi}	1426.6	0.548	8.3	18.6	1424.0	81.4
Water imbibition	87.2	0.402	31.2	67.3	1751.4	32.7
Oil-wet						
100% Water	37.2	0.923				
100% Decane	635.2	0.947				
S_{wi}	462.0	0.617	24.5	21.7	646.4	78.3
Water imbibition	699.9	0.674	26.3	15.8	837.7	84.2

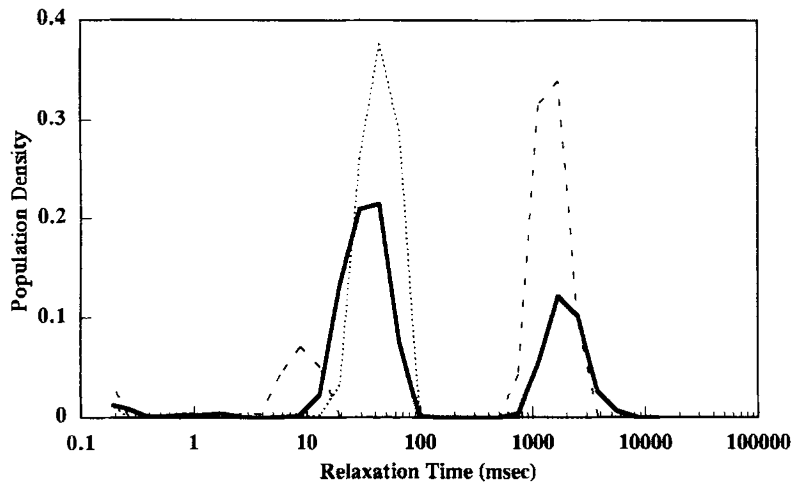

Fig. 1. T_1 distributions for water-wet outcrop chalk at various stages of water flood test. Dotted line = 100% brine saturated; dashed line = saturated with decane at S_{wi}; and solid line = decane and brine-saturated after water-imbibition.

tions of the water-wet chalks. The short relaxation time mode shifts to the 40 ms relaxation time associated with the brine-saturated sample (Fig. 1). NMR intensities again compare favorably with core measurements of water saturation of 60–70% (Fig. 2).

The oil-based mud treated chalks also have a bimodal distribution of relaxation times at S_{wi} (Fig. 3). The mode at 40 ms that is associated with the water

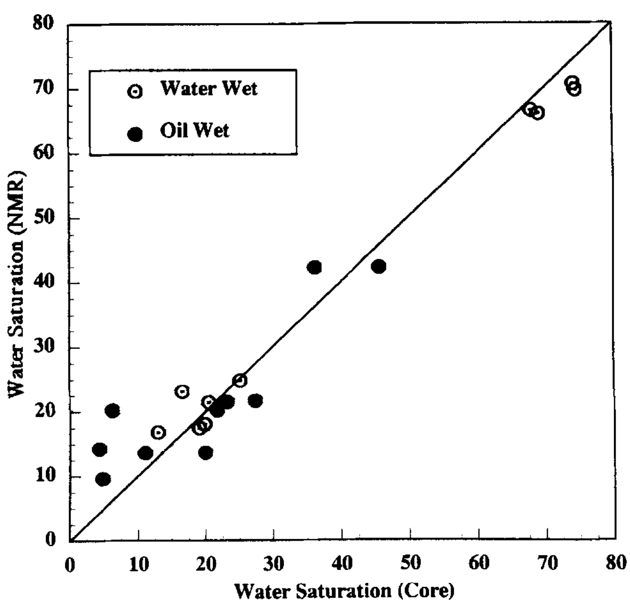

Fig. 2. Comparison of water saturations determined from T_1 distribution peak area and conventional core analysis. Different stages of water-flood test on both water-wet and oil-wet chalks are included.

relaxation corresponds to the relaxation time for 100% brine saturated sample. The decane relaxation mode at 650 ms is identical to the mode for 100% decane saturated oil-wet chalk. Spontaneous brine imbibition produced virtually no water uptake by these chalks, which is reflected by the absence of change in the positions and relative intensities of the two T_1 modes. Forced displacement of water into the oil-wet chalks resulted in water-saturation of 40–50% (Fig. 2) with no change in the positions of the T_1 relaxation modes.

DISCUSSION

Differences in the relaxation time distributions at any stage in the water-flood sequence for the naturally water-wet samples can be explained by differences in the distribution of the wetting surfaces. The long relaxation time mode at S_{wi} for the two outcrop samples is comparable to that for bulk decane, while the short relaxation time mode is less than that for a 100% brine-saturated sample. The 100% brine-saturated sample represents a relative pore size measurement.[6,7] The shift in the water peak to shorter time indicates a decrease in "effective" pore size, in essence the water-filled pores are replaced by thin water films. The long relaxation time corresponds to the value measured for bulk decane. In these samples the decane undergoes only self-relaxation mechanisms, with no interactions with the pore wall. The interpretation then is that decane has replaced much of the water in the chalk pores, but remains in the middle of the pores with minimal contact with the pore walls. This fractional wettability is interpreted as a homogeneous distribution of water-wet and

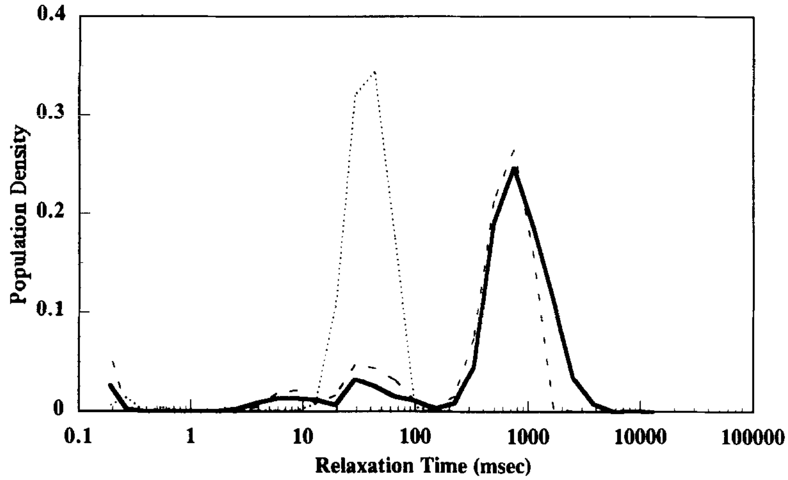

Fig. 3. T_1 distributions for oil-wet outcrop chalk at various stages of water flood test. Dotted line = 100% brine saturated; dashed line = saturated with decane at S_{wi}; and solid line = decane and brine-saturated after water-imbibition.

oil-wet surfaces.[1] With wetting indices of 0.7 and 0.8, most of the pore walls are water-wet and covered with a thin film of water.

The two reservoir samples have long relaxation time modes at S_{wi} less than the T_1 for bulk decane. The short relaxation mode is equal to the T_1 for brine saturated samples. The shift in the longer mode suggests that some of the decane is in contact with pore walls. The short T_1 mode suggests that at least some of the pores are completely filled with water. These samples are interpreted as possessing a mixed wettability state,[9] where there is more organization in the distribution of water-wet and oil-wet pores.

CONCLUSIONS

Relaxation time distributions effectively illustrate the distributions of water and oil in chalks. The intensity of the relaxation time modes are in quantitative agreement with measured water saturations for a range of saturations. Quantitative interpretation of relaxation mechanisms for the oil-based mud treated samples is limited by the presence of paramagnetic ions. When determining fluid saturations, biexponential fitting works fine for chalks because of their uniform pore size. When one measures other sedimentary rocks that have broader pore size distributions these fitting procedures lack sufficient detail to be useful.

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