INTERPRETATION OF WETTABILITY IN SANDSTONES WITH NMR ANALYSIS

Gigi Qian Zhang, Chien-Chung Huang and George J. Hirasaki
Rice University

Abstract:

A systematic interpretation of wettability alteration by NMR analysis was carried out on three types of sandstones with varying shalyness. Two fluid systems were investigated. Soltrol 130 was used as the refined oil. A deep water Gulf of Mexico crude oil was used as the crude oil that is known to alter the wettability in restored state core analysis.

Fluids that are in molecular contact with mineral surfaces have a relaxation time that is less than the bulk fluid relaxation time due to surface relaxation phenomena. Mixed wettability can result in lengthened NMR relaxation of brine compared to 100% brine saturation and shortened NMR relaxation of oil compared to bulk oil when oil becomes in contact with part of the rock surfaces. Thus, NMR T_1 relaxation time distribution provides qualitative description of wettability alteration. Bentheim and Berea were water-wet with refined oil. When saturated with crude oil and brine at S_{wir} they became mixed-wet after aging. After forced imbibition, apparently patches of crude oil remained on the rock surfaces because the residual oil had a shorter relaxation time compared to the bulk oil.

North Burbank sandstone was mixed-wet when either saturated with refined oil at S_{wir} or crude oil after aging. Micropores formed by chlorite flakes were filled with brine. Oil in the macropores was in contact with the tips of chlorite flakes. After forced imbibition, brine in the macropores was partially shielded from the pore walls by a film of oil spanning the tips of chlorite clays. The evidence for this was that macro-brine relaxed slower than 100% brine saturation but faster than bulk brine and oil relaxed faster than bulk oil. Thus North Burbank appeared mixed-wet with either refined oil or with crude oil. However, the extent of wetting change was greater with crude oil. This special wetting behavior of North Burbank came from its microporous structure formed by pore-lining chlorite flakes.

The spontaneous imbibition and forced imbibition wettability test proposed by Amott provides a measurement of wettability. North Burbank sandstone had little spontaneous imbibition with either refined oil or crude oil. Bentheim and Berea sandstones had spontaneous imbibition with refined oil while only Berea had small amount of spontaneous imbibition with crude oil.

Residual oil saturation estimate provides another quantitative indication of wettability alteration. For both refined oil and crude oil systems, North Burbank has significantly less residual oil saturation than that estimated from counter current imbibition. This further confirms that North Burbank was mixed-wet with Soltrol and this crude oil. Berea has the highest residual oil saturation and exhibits about 10 percent reduction of S_{or} from refined oil to crude oil.

Introduction:

Wettability is defined as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Craig, 1971). It has effects on capillary pressure, relative permeability, and residual oil saturation. Knowledge of reservoir wettability is essential to efficient oil recovery processes. Anderson (1986, 1987) gave a comprehensive literature survey on wettability. Salathiel (1973) introduced “mixed wettability” in which the oil-wet surfaces form continuous paths for oil through the larger pores and the smaller pores remain water-wet. Kovscek et al. (1993) developed a pore-level picture of how mixed wettability might form and evolve in reservoir rock initially filled with brine.

Nuclear Magnetic Resonance measurements are sensitive to wettability because of the strong effect that the solid surface has on promoting magnetic decay (relaxation) of contacting fluid. Historically, investigators have applied NMR technique to study wettability on various unconsolidated materials. Brown and Fatt (1956) started the pioneering work by measuring proton spin-lattice relaxation time of water in uncoated sand packs as water-wet porous media, and Dri-film treated sand packs as oil-wet porous media. Saraf et al. (1970) measured spin-lattice relaxation times of glass bead (water-wet) and polymer bead (oil-wet) systems. Williams and Fung (1982) worked on commercial uncoated glass beads as the water-wet system and coated glass beads as the oil-wet system. Hsu et al. (1992) investigated wettability on glass beads. Doughty et al. (1993) investigated on systems of glass or Teflon capillary tubings by NMR microscopy and spin-lattice relaxation.

A lot of research has also been done on consolidated materials. Borgia et al. (1991) studied the relaxation behavior of water-oil in well-characterized microporous porcelain structures. Straley et al. (1991) observed water-wet condition with sandstones partially saturated with kerosene. Hsu et al. (1992) investigated wettability on carbonate cores. Doughty et al. (1993) on Fontainebleau sandstone. Howard and Spinler (1993) observed water-wet condition for chalk cores partially saturated with decane. Øren et al. (1994) conducted two-phase oil-water NMR measurements on sandstones with different wettabilities. Bobroff et al. (1994) investigated on wettability in natural sandstone rocks saturated with deuterium oxide and dodecane. Rueslåtten et al., (1994) observed mixed wettability on North Sea sandstone reservoirs. Morriss et al., (1997) found that Belridge diatomite was water-wet when partially saturated with Soltrol and brine at S_{wir} and predominantly water-wet at native state. Spinler (1997) used NMR for a qualitative estimate of wettability on carbonate field.

In this paper, we will provide a systematic study of wettability on sandstones with either refined oil/brine or crude oil/brine under different saturations. Wettability will be interpreted from NMR T_1 relaxation times and compared with other quantitative methods.

Suite of Test Sandstones:

A suite of sandstones was selected to evaluate the effect of wettability on the NMR response of sandstones. The sandstones were selected based on different degree of shalyness. Their properties are listed in Table 1.

Table 1 Properties of sandstones

Rock Name	Bentheim	Berea	North Burbank
Porosity	22.9±0.4	18.9±0.8	23.1±1.0
Permeability (mD)	3003±20	205±20	237±64
Clays (%)	<1%	3%	chlorite coated

Bentheim sandstone is nearly clay free. Berea sandstone is moderately shaly. Figure 1 provides a view of clays in Berea sandstone at 2000 magnification. The clays are primarily book-like kaolinite and needle-like illite. Berea also contains siderite as localized clusters of crystals. North Burbank sandstone was selected because Trantham and Clampitt (1977) reported that this reservoir was oil-wet due to the iron-rich, chamosite chlorite coating to the sand grains. Figure 2 is the photomicrograph of a North Burbank sand grain showing chlorite coating at 10,000 magnification. Chlorite flakes can be viewed as forming microchannels perpendicular to pore walls such that each micropore opens to macropore (Straley et. al, 1995).

Fig. 1 View of clays in Berea sandstone (Shell Rock Catalog)

Fig. 2 Photomicrograph of North Burbank sand grain showing chlorite coating (adapted from Trantham and Clampitt, 1977).

Berea and North Burbank sandstones have similar porosity and permeability but are very different because of the type of clays. North Burbank sandstone has a significant diffusion effect due to internal field gradient that complicates the interpretation on NMR T_2 measurements (Zhang, et al., 1998). Thus only the T_1 response will be shown to illustrate the effect of wettability.

Test Hydrocarbons:

The effect of wettability on the NMR response was investigated with both refined oil and crude oil. Soltrol 130 is a refined aliphatic oil with a narrow range of molecular weights. A turbidite formation, deep water Gulf of Mexico, 30 °API crude oil was used as a crude oil that is known to alter the wettability in restored state core analysis (Hirasaki, 1996). This crude oil has the code name SMY. The T_2 relaxation time distributions of these two oils are shown in Fig. 3. Soltrol has a narrow, log normal distribution. SMY crude oil has a broad distribution with a tail that extends to relaxation times in the region of BVI (below 33 ms $T_{2cutoff}$). The short relaxation times may be due to an asphaltene content of 3 wt% and 18-24 ppm nickel and 45-48 ppm vanadium.

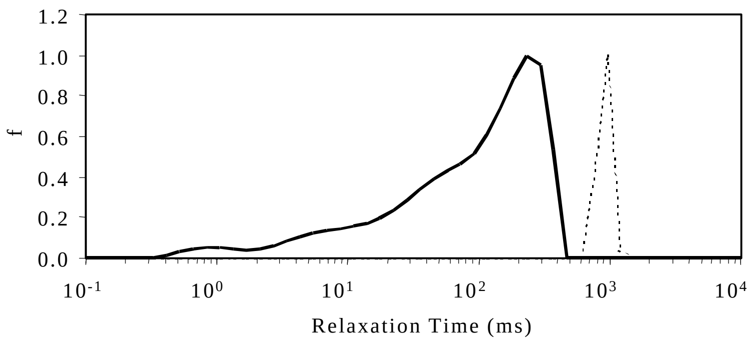

Fig. 3 Normalized T_2 distributions (echo spacing = 0.2 ms) of Soltrol (dotted curve) and SMY crude oil (solid curve).

Wettability Behavior of Refined Oil System:

The sandstone samples were vacuum saturated with 5% NaCl brine to 100% brine saturation, then centrifuged in Soltrol to a capillary pressure of 70 psi. The experiments and NMR measurements were performed on triplicate, Table 2. Because of good consistency, the relaxation time distribution of only one sample of each sandstone will be illustrated. The T_1 relaxation time distributions of Soltrol with brine at S_{wir} are compared with 100% brine saturation for Bentheim, Berea and North Burbank in Fig. 4. T_1 distribution of bulk Soltrol is also shown as the dashed curve.

When the bulk relaxation rate of brine is ignored, brine in 100% S_w rock samples will relax only by surface relaxation mechanism. Thus, T_1 relaxation time distribution represents pore size distribution. The T_1 distribution of North Burbank is bimodal because of a significant amount of microporosity due to chlorite coating.

After centrifuged in Soltrol to 70 psi, Bentheim and Berea have the classic T_1 distribution where the irreducible water response appear at the region corresponding to small pores interpreted from 100% S_w condition. The peak at long relaxation times is Soltrol response. Since the Soltrol peak centers on the T_1 distribution of bulk Soltrol, Bentheim and Berea were water-wet with Soltrol relaxing as bulk fluid.

In North Burbank, irreducible water response has higher peak than the micro-brine response at 100% S_w condition. This is because after drainage with Soltrol, irreducible brine was isolated in each micropore, which no longer had diffusional coupling with macropore brine as in 100% S_w condition (Straley, et al., 1995; Ramakrishnan, et al., 1998). Most importantly, Soltrol peak has shorter relaxation times than bulk Soltrol. Soltrol had surface relaxation as a result of contacting the tips of chlorite flakes. Therefore, North Burbank was mixed-wet with refined oil. Fig. 5 illustrates the fluid distribution in these sandstones after saturated with Soltrol and brine at S_{wir}.

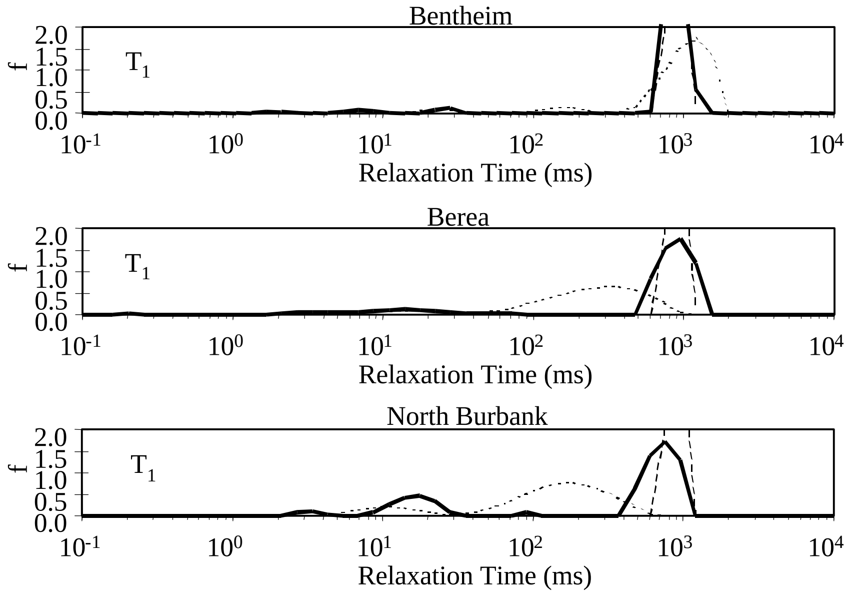

Fig. 4 T_1 relaxation time distributions of the sandstones at 100% brine saturation (dotted curve) and Soltrol saturated to S_{wir} (solid curve). The T_1 relaxation time distribution of bulk Soltrol is shown as the dashed curve.

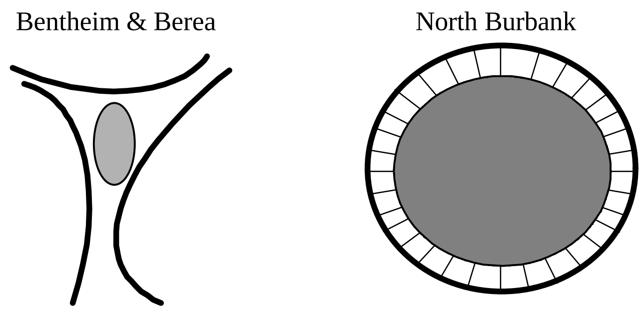

Fig. 5 Fluid distribution of refined oil systems with Soltrol and brine at S_{wir}.

The sandstone samples were then immersed into 5% NaCl brine solution. Only Bentheim and Berea had spontaneous imbibition of brine. Soltrol saturation decreased and brine filled some larger pores. Afterwards, they were centrifuged in brine for forced imbibition to a capillary pressure of –25 psi. Bentheim had greater increase of brine saturation than Berea after forced imbibition. Their T_1 distributions are shown in Fig. 6.

To determine the distribution of residual Soltrol and brine after forced imbibition, rock samples were soaked twice in D_2O brine solution. Water was replaced by D_2O, thus only residual oil will give NMR signal (Morriss, et al., 1997). Fig. 6 compares T_1 distributions after forced imbibition with after D_2O diffusion. The difference in relaxation time distributions is brine response.

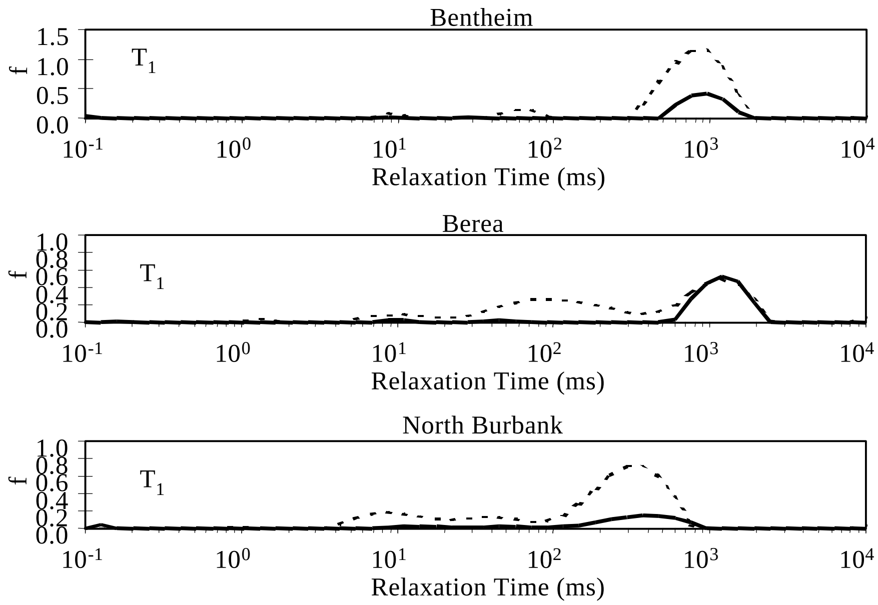

Fig. 6 T_1 relaxation time distributions of the sandstones after forced imbibition (dotted curve) and after D_2O brine diffusion (solid curve).

Wettability behavior for these sandstones after forced imbibition can be determined by comparing distributions after forced imbibition with 100% brine saturation, shown in Fig. 7, and comparing distributions after D_2O brine diffusion with bulk Soltrol, shown in Fig. 8.

In Bentheim, after forced imbibition, brine relaxed similarly to completely water-wet condition with the residual Soltrol response centering on the T_1 distribution of bulk Soltrol. Therefore, Bentheim was water-wet with Soltrol relaxing as bulk fluid.

In Berea, after forced imbibition, although the peak at long relaxation times appears to the right of the distribution of 100% brine saturation, it should not be interpreted as brine relaxing slower than completely water-wet condition due to wettability alteration. This is because from Fig. 6 this peak is mostly residual Soltrol response and it does not have shorter relaxation time than bulk Soltrol as shown in Fig. 8. Therefore, Berea was water-wet too.

In North Burbank, after forced imbibition, the distribution at long relaxation times is to the right of the distribution at 100% brine saturation. It could be due to the brine in macropores relaxing slower than completely water-wet condition, and/or because the residual Soltrol has large bulk relaxation times. However, from Fig. 8, the distribution of residual Soltrol has apparent shift from T_1 distribution of bulk Soltrol, meaning that Soltrol had surface relaxation due to the contact with the tips of chlorite flakes. Hence, North Burbank was mixed-wet, with macro-brine partially shielded from the pore walls by a film of Soltrol spanning the tips of chlorite flakes (Ben Swanson, private communication).

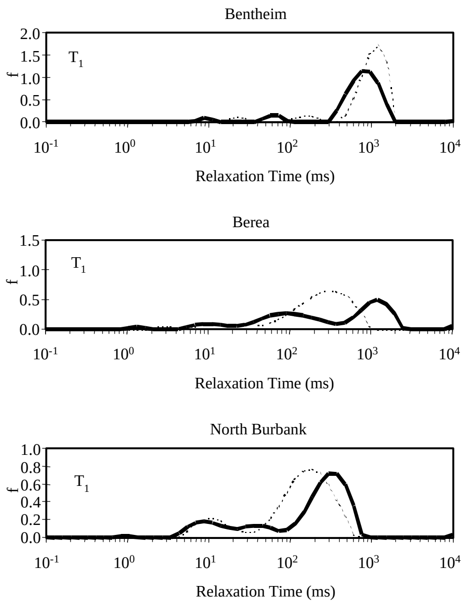

Fig. 7 T_1 relaxation time distributions of the sandstones after forced imbibition (solid curve) compared to 100% brine saturation (dotted curve).

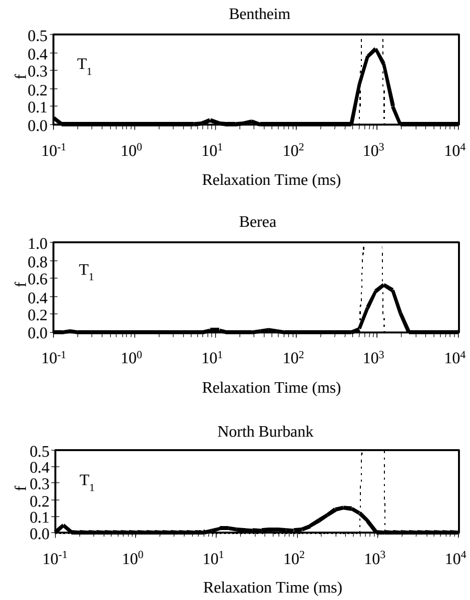

Fig. 8 T_1 relaxation time distributions of the sandstones after D_2O brine diffusion (solid curve) compared to bulk Soltrol (dotted curve).

The distributions of Soltrol and brine after forced imbibition for Bentheim, Berea and North Burbank are illustrated in Fig. 9. Due to the pore lining chlorite, North Burbank was mixed-wet even with refined oil.

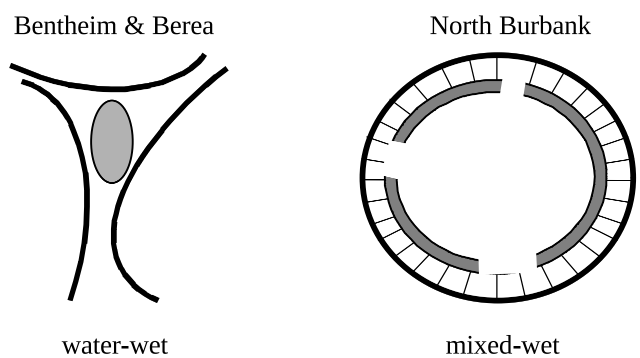

Fig. 9 Fluid distribution of refined oil systems after forced imbibition of brine.

Wettability Behavior of Crude Oil System:

The sandstone samples were cleaned and restored to 100% brine saturation. Then, they were centrifuged in SMY crude oil to a capillary pressure of 70 psi. NMR T_1 measurements were made and then the samples were immersed in a sealed bottle of SMY crude oil, aged for 3 weeks at a temperature of 50 °C. Figure 10 compares the T_1 distributions before aging and after aging. The T_1 distribution of bulk SMY crude oil is scaled to oil saturation. For all three sandstones, before aging, T_1 distributions start from the same position as bulk SMY crude oil. Therefore, they were all water-wet with crude oil relaxing at the bulk rate. After aging, all distributions shift to shorter relaxation times. Bentheim had the greatest surface relaxation of SMY crude oil, Berea in the middle, and North Burbank exhibited the smallest surface relaxation effect. In North Burbank, the peak interpreted as the micro-brine response does not change position and amplitude after aging. Therefore, brine filled micropores all the time and SMY crude oil did not invade into the micropores during aging. In conclusion, all sandstones changed from water-wet to mixed-wet after aging (Rueslåtten, et al., 1994). The distribution of crude oil and brine after aging is illustrated in Fig. 11. Crude oil was either in contact with rock surface in Bentheim and Berea or in contact with the tips of chlorite flakes in North Burbank.

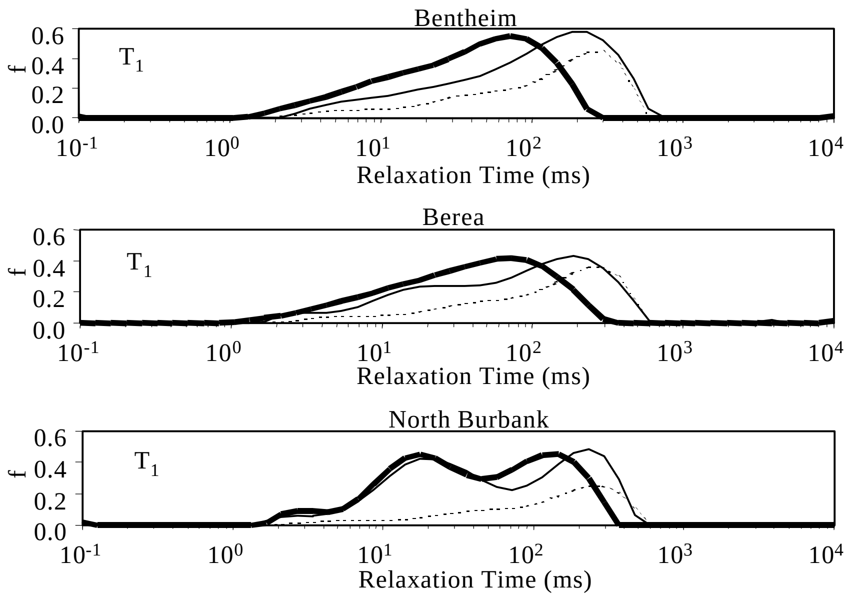

Fig. 10 T_1 relaxation time distributions of the sandstones with SMY crude oil saturated to S_{wir} before aging (solid curve) and after aging (bold solid curve). The T_1 relaxation time distribution of bulk SMY crude oil, scaled to oil saturation, is shown as the dotted curve.

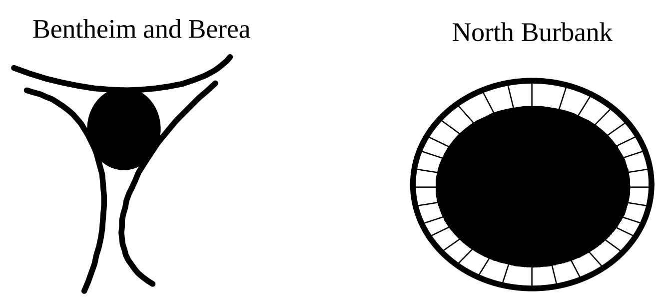

Fig. 11 Fluid distribution of crude oil systems after aging.

In order to prove that the wettability change after aging interpreted from NMR T_1 distributions was not due to chemical change in the bulk crude oil, the T_1 distributions of bulk SMY crude oil before aging and after aging under the same aging condition are compared in Fig. 12. There is negligible difference between the T_1 distributions before aging and after aging. Therefore, aging did not result in any chemistry change of SMY crude oil itself.

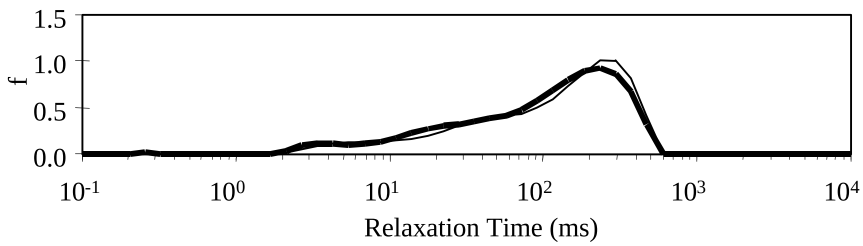

Fig. 12 T_1 relaxation time distributions of bulk SMY crude oil before aging (solid curve) and after aging (bold solid curve).

Following the same experimental procedures of refined oil systems, the sandstone samples were then soaked in 5% NaCl brine solution for spontaneous imbibition. Only Berea had small amount of spontaneous imbibition. This is due to its least severe wettability alteration to mixed wettability. Figure 13 compares T_1 distributions after forced imbibition of brine with after D_2O diffusion. The difference between the two curves is brine response. Therefore, brine was in large pores of Bentheim, large to medium pores of Berea, and micropores and macropores of North Burbank.

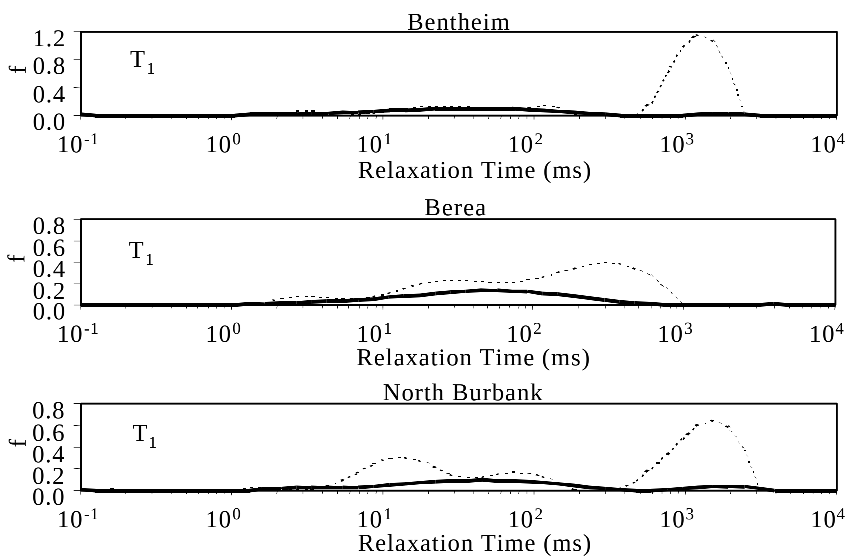

Fig. 13 T_1 relaxation time distributions of the sandstones after forced imbibition (dotted curve) and after D_2O brine diffusion (solid curve).

Figure 14 compares T_1 relaxation time distributions after forced imbibition of brine with 100% brine saturation. For Bentheim and Berea, the water peak after forced imbibition appears at similar range of relaxation times as 100% brine saturation. However, for North Burbank, the macropore brine relaxes slower than 100% brine saturation and faster than bulk brine. This is interpreted as the macro-brine was partially shielded from pore walls by a film of SMY crude oil spanning the tips of chlorite flakes.

Residual oil response after D_2O brine diffusion is compared with T_1 distribution of bulk oil in Fig. 15. For all three sandstones, residual oil has surface relaxation due to wettability alteration. The small peaks at long relaxation times are due to incomplete exchange of water by D_2O.

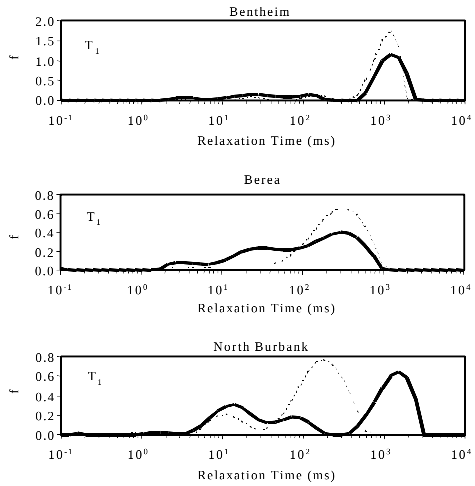

Fig. 14 T_1 relaxation time distributions of the sandstones after forced imbibition (solid curve) compared to 100% brine saturation (dotted curve).

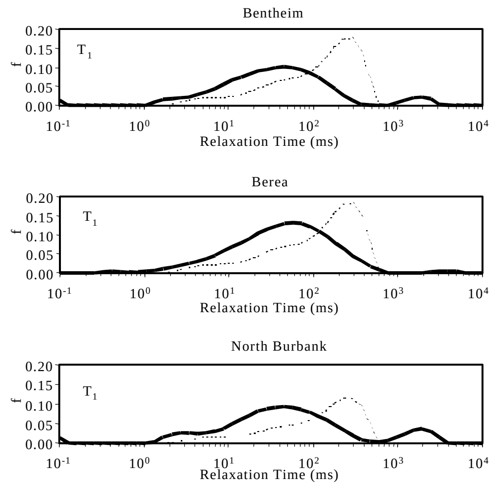

Fig. 15 T_1 relaxation time distributions of the sandstones after D_2O brine diffusion (solid curve) compared to bulk SMY crude oil (dotted curve), scaled to oil saturation.

Therefore, after forced imbibition of brine, all three sandstones became mixed-wet (Salathiel, 1973; Kovscek et al., 1993). As shown in Fig. 16, patches of crude oil was in contact with sand grains in Bentheim and Berea, and residual SMY crude oil spanned part of the tips of chlorite clays in North Burbank.

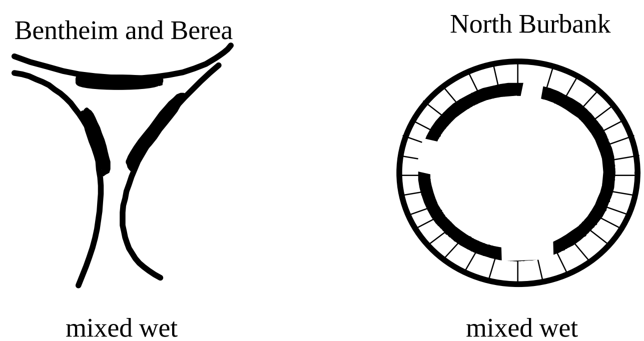

Fig. 16 Fluid distribution of crude oil systems after forced imbibition of brine.

Amott Water Wettability Index:

Amott water wettability index (Anderson, 1986) was determined by dividing the amount of oil displaced by brine by spontaneous imbibition with the amount of oil displaced by brine by both spontaneous and forced imbibition. Water-wet systems have Amott water wettability index about 1. Both intermediate-wet and oil-wet systems have Amott index value around 0.

Table 2 lists the Amott index values for Bentheim, Berea and North Burbank for refined oil and crude oil systems.

Table 2 Irreducible brine saturation, brine saturation after spontaneous imbibition and after forced imbibition determined by weighting for Bentheim, Berea and North Burbank. Amott water wettability index values were determined from these values.

	Soltrol/Brine					SMY Crude Oil/Brine				
S_brine	S_{wir}	Sp.	For.	Amott	Avg.	S_{wir}	Sp.	For.	Amott	Avg.
Bentheim-1	8.3	58.4	73.0	0.77	0.77	13.6	28.4	75.9	0.24	0.20
Bentheim-2	2.0	51.8	67.1	0.77	±0.01	1.5	15.8	68.4	0.21	±0.05
Bentheim-3	5.5	55.3	69.5	0.78		4.5	13.1	67.6	0.14	
Berea-1	17.9	55.5	56.5	0.97	1.05	31.2	53.8	72.7	0.54	0.54
Berea-2	17.8	52.0	48.2	1.13	±0.08	24.7	44.6	60.7	0.55	±0.01
Berea-3	19.2	50.7	49.1	1.06		28.7	47.1	62.8	0.54	
North Burbank-1	41.4	42.6	85.3	0.03	0.04	52.1	50.5	88.5	-0.04	-0.04
North Burbank-2	45.7	47.2	86.5	0.04	±0.01	59.7	55.4	95.5	-0.12	±0.08
North Burbank-3	40.8	43.7	92.5	0.05		50.9	52.7	91.4	0.04	

For refined oil systems, Bentheim and Berea had spontaneous imbibition and they were water-wet. North Burbank was mixed-wet. For crude oil systems, after aging, only Berea had small amount of spontaneous imbibition and all three sandstones were mixed-wet. Unlike intermediate-wet, which means a contact angle between 70° and 110°, and oil-wet, which corresponds to a contact angle between 110° and 180°, mixed wettability refers to nonuniform distribution of water and oil on rock surfaces. Even though Amott water wettability index only distinguishes water-wet condition, it indicates the same wettability alteration as those inferred from NMR distribution interpretation.

Residual Oil Saturation:

Residual oil saturation provides another quantitative indication of wettability alteration. Residual oil saturation for refined oil and crude oil systems are determined by averaging S_{or} from weighting and NMR measurements after forced imbibition and after D_2O brine diffusion. Measurements of counter current imbibition (CCI) of Toluene-air system were performed at 25%, 50%, 75% and 90% initial air saturations. Plots of residual air saturation vs. initial air saturation are prepared. Since Toluene-air system provides strongly wetting behavior, residual oil saturation corresponding to initial oil saturation with brine at S_{wir} can be inferred for strongly water-wet system. Figure 17 compares residual oil saturation for Bentheim, Berea and North Burbank. The white bars are CCI residual, hashed bars are S_{or} for Soltrol and shaded bars are for SMY crude oil. ‘w’ denotes water-wet condition and ‘m’ denotes mixed-wet condition.

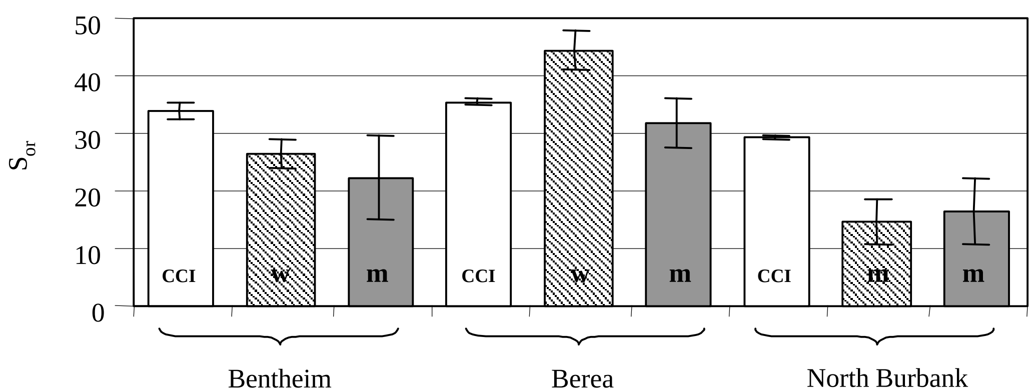

Fig. 17 Residual oil saturation from CCI (white bars), refined oil systems (hashed bars) and crude oil systems (shaded bars).

For Bentheim and Berea, Soltrol has higher residual oil saturation than SMY crude oil because the sandstones were water-wet with refined oil while mixed-wet with crude oil. For North Burbank, refined oil has similar S_{or} as crude oil because they were both mixed-wet. For both refined oil and crude oil systems, North Burbank has the smallest S_{or} due to its strongest mixed-wet condition. Berea has the highest S_{or} and has a 10% reduction of S_{or} from refined oil system to crude oil system. Bentheim, Berea and North Burbank have similar CCI residual because it predicts the residual oil saturation when the rock is strongly water-wet. For North Burbank, CCI residual is significantly higher than S_{or} of refined oil and crude oil systems. This positively confirms that North Burbank is even mixed-wet with refined oil.

Conclusions:

NMR T_1 measurement is an effective tool in analyzing wettability alteration. Together with Amott wettability index and residual oil saturation estimate, they give consistent description of wettability condition of core samples under various conditions. Bentheim and Berea were water-wet with refined oil, but became mixed-wet with crude oil after aging. Due to the chlorite lining of North Burbank, it was mixed-wet even with refined oil.

Acknowledgments:

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