### NMR STUDY ON PORE OCCUPANCY AND WETTABILITY MODIFICATION DURING LOW SALINITY WATERFLOODING

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#### ABSTRACT

In the last decade, the benefits of injecting low salinity water have been recognised by BP from the core to the reservoir scale and led to BP's commercial *LoSal*<sup>TM</sup> EOR process. Via these studies, BP demonstrated that Multi-component Ion Exchange (MIE) is the underlying mechanism.

In this paper, pore occupancy and wettability modification during low salinity water EOR process have been investigated by NMR techniques, for the first time. New NMR wettability indices and wettability index modification factors have been proposed and a mixed-wetting NMR signature after water flooding has been identified. The proposed NMR approaches have been applied to determine pore occupancy and wettability changes during core ageing, spontaneous imbibition, and water flooding with injection waters of different salinities. By comparing experimental results with the high salinity brine spontaneous imbibition and core flood, we show that the wettability of reservoir rocks has been modified to an increased water wet state by brine invading with different low salinities through pore-corners and pore-centres and stripping out adsorbed crude oil from pore surface.

#### **INTRODUCTION**

The concept of low salinity injection for improving oil recovery in sandstone reservoirs has been studied since the early 1990's in various laboratories [1-7]. BP has led the development and commercialisation of the technology as BP's  $LoSal^{TM^*}$  EOR process. A number of successful field trials, at single well and well to well scale [8-12] have also been completed. Through these lab and field studies, BP has demonstrated that the underlying oil release mechanism is Multi-component Ion Exchange (MIE), via expansion of the electrical double layer at clay particle surface [6], leading to wettability change.

Wettability is often defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. Mixed-wettability is defined as waterwet and oil-wet surfaces coexist within a single pore of a porous medium. Wettability

<sup>\*</sup> *LoSal* is a trade mark of BP plc

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controls the fluid distribution in a reservoir and therefore exerts a fundamental influence on flow behaviours, residual oil saturation and relative permeability and ultimately has a fundamental influence on reservoir performance.

NMR wettability [13-16] and pore occupancy [17] measurement is a non-intrusive method which does not interfere with fluid distributions within the porous rock. It can therefore be applied to monitoring on-going dynamic processes such as core ageing, waterflood and EOR processes.

The principal mechanism of NMR wettability determination is based on the fact that the relaxation time of the wetting phase becomes shorter compared to the bulk phase, due to surface relaxation. However, for multiphase fluids in porous rock, the distribution of NMR relaxation time comprises superimposed information regarding microscopic fluid distribution, fluid saturation, pore structure, rock mineralogy, and distribution of paramagnetic impurities on the pore surface, as well as the crude oil composition.

This paper shows that in order to decouple the superimposed information in the NMR relaxation time distribution, it is necessary to propose new NMR wettability indices and wettability index modification factors for low salinity waterflooding processes. The proposed NMR approach has been applied to determine pore filling mechanisms and wettability changes during core ageing, spontaneous imbibition, and water flooding with injection waters of different salinities. By comparing these indices with spontaneous imbibition and core flood with high salinity brine, we show that the wettability of reservoir rock has been modified to an increased water wet state by using low salinity brines.

# NMR RELAXATION TIME, PORE OCCUPANCY AND WETTABILITY

The spin-spin relaxation time of a fluid-saturated porous rock is affected by three mechanisms [18]: (i) relaxation of the bulk fluid; (ii) surface relaxation of the fluid at the pore surface; and (iii) relaxation owing to self diffusion of the fluid in a magnetic field gradient. When applying low field NMR for spin-spin relaxation time measurement, the induced internal magnetic gradient in the porous medium is very small [19]. As a short echo time is employed, the contribution of self diffusion to spin-spin relaxation time can be negligible. In this paper, it is assumed that water and oil saturated porous rocks are in the fast diffusion regime [20]. Hence, for a 100% water-saturated porous rock, the inverse of the spin-spin relaxation time ( $T_2$ ) of the water phase can be expressed as:

$$\frac{1}{T_{2,W1}} = \rho_{2,W} \frac{A}{V} + \frac{1}{T_{2B,W}}$$
(1)

Where  $T_{2,W1}$  is the spin-spin relaxation time of fully water saturated porous rock,  $S_w$  represents water phase saturation,  $\rho_{2,w}$  is the spin-spin relaxivity of the water phase,  $T_{2B,W}$ 

is the bulk spin-spin relaxation time of the water phase, A is the surface area of the pores and V is the pore volume.

For a 100% oil-saturated porous medium, the inverse of the spin-spin relaxation time  $(T_2)$  of the oil phase can be expressed as:

$$\frac{1}{T_{2,01}} = \rho_{2,0} \frac{A}{V} + \frac{1}{T_{2B,0}}$$
(2)

Where  $T_{2,O1}$  is the spin-spin relaxation time of fully oil saturated medium,  $\rho_{2,O}$  is the spin-spin surface relaxivity of the oil phase,  $T_{2B,O}$  is the bulk spin-spin relaxation time of the oil phase, A is the surface area of the porous medium and V is the pore volume.

During primary drainage process, an initial fully water saturated and strong water-wet porous rock is de-saturated by crude oil. If the applied capillary pressure exceeds the threshold capillary pressure of a given pore, the oil phase will invade the pore and displace water from the central portion of the pore. With further increase of capillary pressure, remained irreducible water is in the corners of the pore and as thin water film coating the surface of the pore walls. The threshold capillary pressure is related to pore geometry and relaxation time  $T_2$  cut-off. This cut-off can be applied to partition the pore size distribution into oil invaded larger pores and 100% water saturated smaller pores after primary drainage.

For reservoir rocks, wettability alteration mainly occurs in crude oil invaded larger pores after primary drainage. Therefore, the evaluation of wettability alteration focuses mainly on these larger pores. For a 100% oil-saturated porous rock, the inverse of the spin-spin relaxation time ( $T_{2,01,L}$ ) of the oil phase in these pores can be expressed as:

$$\frac{1}{T_{2,01,L}} = \rho_{2,0} \frac{A_L}{V_L} + \frac{1}{T_{2B,0}}$$
(3)

Where  $A_L$  is the surface area of the larger pores and  $V_L$  is the volume of the larger pores.

At initial oil saturation conditions, the inverse of the spin-spin relaxation time  $(T_2)$  of the oil phase in these larger pores can be expressed as:

$$\frac{1}{T_{2,o,L}(S_{oi})} = \rho_{2,Oi} \frac{A_{oi,L}}{V_L S_{oi,L}} + \frac{1}{T_{2B,O}}$$
(4)

Where  $T_{2,O,L}(S_{Oi})$  is the spin-spin relaxation time of the oil phase in oil invaded larger pore at initial oil saturation condition,  $S_{Oi,L}$  represents initial oil phase saturation as a fraction of pore volume of the oil invaded larger pores,  $\rho_{2,Oi}$  is the spin-spin surface relaxivity of the oil phase at initial oil phase saturation,  $A_{oi,L}$  is the surface area of the larger pores contacted by oil phase, and  $V_L$  is the pore volume of the larger pores.

At initial oil saturations (Soi), the oil wettability index ( $WI_{Oi,L}$ ), for the oil phase invaded larger pores is defined by combining Equations (3) and (4) as:

$$WI_{Oi,L} = \frac{\rho_{2,Oi}A_{Oi,L}}{\rho_{2,O}A_L} = \frac{\left[\frac{1}{T_{2,O,L}(S_{Oi})} - \frac{1}{T_{2B,O}}\right]S_{Oi,L}}{\frac{1}{T_{2,O1,L}} - \frac{1}{T_{2B,O}}}$$
(5)

The defined NMR wettability is based on two factors, i.e., the fraction of the pore surface in direct contact with the fluid  $(\frac{A_{Oi,L}}{A_L})$ , and the surface relaxivity ratio  $(\frac{\rho_{2,Oi}}{\rho_{2,O}})$ . The defined surface relaxivity ratio eliminates the influence of other factors on the surface relaxivity, (e.g., rock mineralogy and paramagnetic impurities that are present on the pore surface), and is directly related to the affinity between the pore surface and the fluids that are present in the pore space. The defined oil phase wettability index values range between 0 (strong water wet) and 1 (strong oil wet), and a decimal fraction of wettability index represents a mixed-wet state. Equivalent water phase wettability index can also be defined.

Similarly, at a residual oil saturation (Sor), after imbibition, waterflooding, or EOR, oil phase wettability index ( $WI_{Or,L}$ ) for these larger pores is defined as:

$$WI_{Or,L} = \frac{\rho_{2,Or}A_{Or,L}}{\rho_{2,O}A_L} = \frac{\left[\frac{1}{T_{2,O,L}(S_{Or})} - \frac{1}{T_{2B,O}}\right]S_{Or,L}}{\frac{1}{T_{2,O1,L}} - \frac{1}{T_{2B,O}}}$$
(6)

Where  $T_{2,O,L}(S_{Or})$  is the spin-spin relaxation time of the oil phase in oil invaded larger pore at residual oil saturation,  $\rho_{2,Or}$  is the spin-spin surface relaxivity of the oil phase at residual oil phase saturation,  $A_{Or,L}$  is the surface area of the larger pores contacted by oil phase, and  $S_{Or,L}$  is residual oil saturation as a fraction of the pore volume of the larger pores.

After waterflood, the inverse of the spin-spin relaxation time  $(T_2)$  of the water phase can be expressed as:

$$\frac{1}{T_{2,W}(Sor1)} = \rho_{2,W1} \frac{A_{W1}}{VS_{W1}} + \frac{1}{T_{2B,W1}}$$
(7)

Where  $T_{2,W}(S_{or1})$  is the spin-spin relaxation time of the water phase at residual oil saturation,  $S_{or1}$ , after the waterflood,  $\rho_{2,w1}$  is the spin-spin surface relaxivity of the water phase after the waterflood,  $T_{2B,W1}$  is the bulk spin-spin relaxation time of the water phase after water flood,  $A_{W1}$  is the surface area of the pores that is in contact with the water phase after the waterflood,  $S_{W1}$  is the water saturation after the waterflood and V is the pore volume.

After an EOR process, the inverse of the spin-spin relaxation time  $(T_2)$  of the water phase can be expressed as:

$$\frac{1}{T_{2,W}(Sor2)} = \rho_{2,W2} \frac{A_{W2}}{VS_{W2}} + \frac{1}{T_{2B,W2}}$$
(8)

Where  $T_{2,W}(S_{or2})$  is the spin-spin relaxation time of the water phase at a residual oil saturation,  $S_{or2}$ , after the EOR flood,  $\rho_{2,w2}$  is the spin-spin surface relaxivity of the water phase after the EOR process,  $T_{2B,W2}$  is the bulk spin-spin relaxation time of the water phase after EOR process,  $A_{W2}$  is the internal surface area of the pores that is in contact with the water phase after the EOR flood,  $S_{W2}$  is the water saturation after the EOR flood and V is the pore volume.

By combining Equation (7) with Equation (8), an NMR wettability index modification factor (WIMF<sub>w</sub>) is defined for the water phase, which compares an EOR process with a water flood process:

$$WIMF_{W} = \frac{\rho_{2,W2}A_{W2}}{\rho_{2,W1}A_{W1}} = \frac{\left[\frac{1}{T_{2,W}(Sor2)} - \frac{1}{T_{2B,W2}}\right]S_{W2}}{\left[\frac{1}{T_{2,W}(Sor1)} - \frac{1}{T_{2B,W1}}\right]S_{W1}}$$
(9)

#### EXPERIMENTS, RESULTS AND DISCUSSIONS

#### **Experiment 1: NMR Studies for Core Ageing and Spontaneous Imbibition with Low** Salinity Water and High Salinity Seawater

#### **Experimental Protocol of Experiment 1**

Two sandstone reservoir core plugs #156 and # 157 with similar perm porosity and mineralogy were selected as a pair. The plugs were cleaned using a flow through method with hot solvents. The core plugs had a porosity of 0.15 and a permeability of 25 mD. The two core plugs of #156 and #157 were fully saturated with reservoir formation brine with a concentration of 14.6 g/l., and desaturated to initial water saturations ( $S_{wi}$ ) of 0.21 and 0.20, respectively, by nitrogen gas using the confined porous plate technique with capillary pressure of 182psi. The two core plugs were then saturated with kerosene at

initial water saturation condition. Reservoir crude oil was injected into the core plugs at the reservoir temperature of 68°C via a filter of 0.5 micron. Prior to the injection of the crude oil, the kerosene was displaced by a buffer of toluene to prevent deposition of asphaltenes from the crude oil which can otherwise occur if crude oil contacts kerosene. The two core plug samples at initial water and oil saturation condition were then aged at a temperature of 68°C for a period of three weeks. A 1.5 pore volume of crude oil was refreshed weekly during the ageing period.

NMR spin-spin relaxation time measurements were carried out for the two core plugs at different saturation conditions by employing CPMG pulse sequence with 0.2ms echo time using 2MHz NMR instrument. The obtained CPMG data were inverted to a  $T_2$  relaxation time distribution using an inverse Laplace transformation algorithm.

Following core ageing, the two core plugs were placed in imbibiometers. Core plug #156 was submerged in low salinity brine and core plug #157 was submerged in synthetic seawater with a salinity of 40.4 g/l. The imbibiometers were placed inside a laboratory oven and were maintained at a temperature of 68°C. The oil produced due to spontaneous imbibition was monitored.

The low salinity brine was obtained by diluting the synthetic seawater with deionised water such that the total dissolved solids content was 1500ppm.

#### **Results and Discussions of Experiment 1**

The two brine imbibition experiments showed that the water saturation level rose faster and reached a higher final water saturation value of 46.4% for the low salinity brine with core plug #156 than final water saturation of 42.2% for the high salinity brine with core plug #157 after 42 days spontaneous imbibition.

Figure 1 shows that the  $T_2$  relaxation time distributions for sister rock core plugs # 156 and#157 at 100% formation water saturation are almost identical indicating that the two plugs have very similar pore size distributions.

Figure 2 and Figure 3 show relaxation time ( $T_2$ ) distributions for a bulk crude oil (labelled Bulk crude) and for core plugs of #156 and #157 at different saturation states i.e. at 100% brine saturation (labelled Sw1), at 100% oil saturation (labelled So1), at initial oil and water saturation before ageing (labelled Swi) and after ageing for three weeks (labelled Aged@Swi), and after spontaneous brine imbibition (labelled as Imbibition). In Figures 2 and 3, the relaxation time  $T_2$  distributions for core plug #156 and #157 before and after ageing all show bimodal distributions, the upper mode mainly reflects initial oil phase in the larger pores, the lower mode mainly reflects initial water phase in smaller pores. The  $T_2$  distribution of initial crude oil phase in the larger pores showed that the aged rock sample was shorter than for the un-aged rock sample. This arises because the oil phase contacts the surface of the pore walls and results in wettability alteration to mixed- wet state in the larger pores.

The results presented in Figure 2 show that the  $T_2$  relaxation time distributions at initial water and oil saturation before and after core ageing were almost unchanged for  $T_2$  relaxation time components less than 2.5ms. These components mainly reflect  $T_2$  relaxation time distributions of 100% initial water saturated smaller pores, these smaller pores remain strongly water-wet after core ageing, and therefore their relaxation time distributions did not change after core ageing. Applying a  $T_2$  relaxation time cut-off ( $T_{2C}$ ) of 2.5ms to the relaxation time  $T_2$  distribution at initial water and oil saturation before ageing and relaxation time distribution of bulk crude oil, the determined 100% initial water saturated smaller pores is 0.14PV, the initial water in the corners and as water films at pore surface of oil invaded larger pores can be calculated as  $S_{Oi,L}$ =0.92. Very similar phenomena have been observed for core plug #157 in Figure 3 with determined  $T_{2C}$  of 3.3ms, and 100% initial water saturated smaller pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded larger pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded smaller pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded larger pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded larger pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded larger pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded larger pores is 0.16PV, and initial water in the corners and as water film at pore surface of oil invaded larger pores of 0.04PV, and  $S_{Oi,L=}$  0.95, which suggests that Swi distribution between the two samples was very similar.

The peak values of  $T_2$  relaxation time distributions of the oil phase for core plugs #156 and #157 at initial oil saturation after aging ( $T_{2,O,L}(Soi)$ ), at 100% oil phase saturation ( $T_{2,O1,L}$ ) as well as the peak value of relaxation time ( $T_2$ ) for a bulk crude oil sample ( $T_{2B,O}$ ) and the values of initial oil saturation ( $S_{oi,L}$ ) as a fraction of pore volume of the oil phase invaded larger pores are shown in Table 1 and 2, respectively:

•	able 1: The peak values of $I_2$ and $S_{oi,L}$ value for plug #15				
	T <sub>2B,O</sub>	T <sub>2,01,L</sub>	T <sub>2,O,L</sub> (Soi)	S <sub>oi,L</sub>	
	(ms)	(ms)	(ms)		
	50.2	26.6	31.9	0.92	

Table 1: The peak values of  $T_2$  and  $S_{oi,L}$  value for plug #156

Ľ	able 2: The	peak values of $T_2$	and Soi, L value	for plug #15	7
	T <sub>2B,O</sub>	T <sub>2,01,L</sub>	T <sub>2,O,L</sub> (Soi)	Soi,L	
	(ms)	(ms)	(ms)		

38.3

50.2

29.1

0.95

Using the determined initial oil saturation values and peak values of  $T_2$  distributions shown in Table 1 for plug #156 and Table 2 for plug #157 as inputs into Equation (5), the wettability index for the oil phase in the larger pores after aging was calculated to be  $WI_{oi,L}$  of 0.60 for plug #156, and  $WI_{oi,L}$  of 0.41 for plug #157, which shows a mixed-wet state.

In Figures 2 and 3, the relaxation time  $T_2$  distributions for both core plugs #156 and #157 after spontaneous brine imbibition also show bimodal distributions. Comparing with the  $T_2$  distributions at initial saturation condition, the amplitude of upper mode decreased significantly, which is due to oil phase produced from the larger pores. At the same time, the amplitude of lower mode increased significantly and the peak  $T_2$  value of the lower

mode increased slightly. This is due to increase of water volume in the corners of these larger pores by capillary force during spontaneous brine imbibition.

Table 3 shows the peak values of  $T_2$  of the oil phase for core plug sample #156 at residual oil saturation after spontaneous low salinity brine imbibition ( $T_{2,O,L}(Sor)$ ) and at the 100% oil phase saturation ( $T_{2,O,L}$ ). In addition the peak value of  $T_2$  for a bulk crude oil sample ( $T_{2B,O}$ ) and the value of residual oil saturation ( $S_{or,L}$ ) as a fraction of pore volume of the oil phase invaded larger pores after spontaneous low salinity brine imbibition are included.

		- 01,L	1 0
T <sub>2B,O</sub>	T <sub>2,01,L</sub>	$T_{2,O,L}(Sor)$	
(ms)	(ms)	(ms)	S <sub>or,L</sub>
50.2	26.6	50.2	0.62

Table 3: The peak values of  $T_2$  and  $S_{or,L}$  values for plug # 156

The data in Table 3 and Equation (6) was used to calculate the NMR oil phase wettability index for core plug sample #156 at Sor after spontaneous low salinity brine imbibition. This gave an oil phase wettability index of 0, indicating a strongly water wet state.

Table 4 shows the peak values of  $T_2$  relaxation times of oil phase for core plug sample #157 at residual oil saturation after spontaneous high salinity seawater imbibition  $(T_{2,O,L}(Sor))$  and at 100% oil phase saturation  $(T_{2,O,L})$ . In addition the peak value of relaxation time  $(T_2)$  for a bulk crude oil sample  $(T_{2B,O})$  and the value of residual oil saturation  $(S_{or,L})$  in the larger pores after spontaneous high salinity seawater imbibition are also included.

tore 4. The peak values of $T_2$ and $S_{or,L}$ values for plug $\# T$				
T <sub>2B,O</sub>	T <sub>2,01,L</sub>	$T_{2,O,L}(Sor)$		
(ms)	(ms)	(ms)	S <sub>or,L</sub>	
50.2	29.1	41.9	0.69	

Table 4: The peak values of  $T_2$  and  $S_{or,L}$  values for plug # 157

The NMR oil phase wettability index for core plug sample #157 at residual oil saturation, post spontaneous sea water imbibition, can be calculated using Equation (6) and data in Table 4, which gives the oil phase wettability index of 0.19, indicating a mixed wet state.

The NMR studies of the pair of core plugs #156 and #157 show that low salinity brine spontaneous imbibition results in a increased water wet state than sea water imbibition by invading larger pores through the pore-corners and stripping out adsorbed crude oil from pore surface, and consequently increased oil recovery.

## **Experiment 2: NMR Studies for Water flood with High Salinity Brine and Different Low Salinity Brines**

#### **Experimental Protocol of Experiment 2**

In this experiment, waterflood experiments were carried out on three sister core plug samples using different salinity brines as injection water. The permeability of the core plugs was 158mD, and porosity was 0.26. According to similar experimental procedures described in the experiment 1, the core plugs were prepared and aged at an initial water formation saturation of 17.6%. NMR measurements were then conducted.

The first of the three sister core plugs was subjected to a high salinity formation water flood with TDS of 33.4g/l. The second of the three sister core plugs was subjected to a low salinity brine #1 water flood, with TDS of 3.1g/l. The third of the three sister core plugs was subjected to a low salinity brine #2 water flood, with TDS of 0.4g/l.

#### **Results and Discussions of Experiment 2**

Figure 4 shows the T<sub>2</sub> relaxation time distributions for the following states: (i) bulk STO; (ii) one of the core plugs at 100% water saturation (labelled SW1) (iii) one of the core plugs after ageing at initial water and oil saturation (labelled Aged@Swi); (iv) the first sister plug at residual oil saturation after high salinity water flood (labelled High salinity Sor); (v) the second sister plug at residual oil saturation after low salinity brine #1 water flood (labelled Low salinity #1 Sor); and (vi) the third sister plug at residual oil saturation after low salinity brine #2 water flood (labelled Low salinity #2 Sor).

Figure 4 clearly shows that the main components of the  $T_2$  distribution of the aged core plug has been shifted to the left hand side in comparison with the  $T_2$  distribution of the bulk STO, due to development of mixed wetting state after core ageing with crude oil.

The three  $T_2$  distributions for the three sister core plugs after their respective water floods show significant shape changes from the  $T_2$  relaxation time distribution of the aged sample with significant reduction of oil peaks and the emergence of additional peaks on the right hand side. The new additional components have  $T_2$  values larger than the longest  $T_2$  value (160ms) for bulk STO and for 100% water saturated core plug. These components, therefore, clearly result from the water invasion in centre of larger pores and show a mixed-wetting state signature in the larger pores after water flood. Since the surface areas accessible to the injected water in the centre of larger pores have been limited by oil-wetted surfaces, therefore, the T2 values of the injected water in the centre of the larger pores are between T2 value of bulk water and peak T2 value of fully water saturated core plug.

Thus, the logarithmic mean values of relaxation time distributions, longer than 160ms, are calculated, for high salinity water flood, low salinity #1 water flood, and low salinity #2 water flood, respectively. Therefore, after water flooding these components of the  $T_2$  distribution must arise from the injected water phase displacing oil phase in the centre of the larger pores.

Applying the T<sub>2</sub> cutoff of 160ms to the T<sub>2</sub> distributions to partition the pore volume, the pore volume and logarithmic mean T2 value (T<sub>2</sub>>160ms) of invading water through porecentres is  $S_{W1}=0.209PV$ ,  $T_{2w}(Sor1)=580ms$ ,  $S_{W2}=0.221PV$ ,  $T_{2w}(Sor2)=446ms$ , and  $S_{W3}=0.239PV$ ,  $T_2(Sor3)=393ms$  for high salinity water flood, low salinity #1 water flood, and low salinity #2 water flood, respectively. Inputting the determined T<sub>2</sub> values, water saturation values into Equation (9) and comparing with the high salinity water flood, the calculated water phase wettability index modification factors (WIMF<sub>w</sub>) for the invading water in the centre of the larger pore were 1.47 and 1.86 for low salinity #1 water flood and low salinity #2 water flood, respectively.

The residual oil saturations were determined by core flood are  $S_{or1}$  of 0.469,  $S_{or2}$  of 0.321, and  $S_{or3}$  of 0.224, which corresponds to total water saturations  $S_{wor1}$  of 0.531,  $S_{wor2}$  of 0.679, and  $S_{wor3}$  of 0.776 for high salinity water flood, low salinity #1 water flood, and low salinity #2 water flood, respectively.

After the invading water saturation ( $S_{w\_Centre}$ ) in the center of larger pores has been determined, the invading water saturation ( $S_{w\_Corner}$ ) in the corners of the larger pores after water flood can be calculated by the Equation (10) as 0.146PV, 0.282PV and 0.361PV for high salinity water flood, low salinity #1 water flood, and low salinity #2 water flood, respectively. This shows significant increase of oil recovery by lower salinity water flood through pore-corner filling mechanism.

$$S_{w\_Corner} = S_{wor} - S_{w\_Centre} - S_{wi}$$
(10)

By assuming that predominant  $T_2$  of invaded water through the corners of the larger pores is identical for different salinity brine and inputting the determined water saturation values of invaded water in the corners of large pores into Equation (9), the water phase wettability index modification factors (WIMF<sub>w</sub>) were calculated. Results of WIMF<sub>w</sub> were 1.93 and 2.48 for low salinity #1 water flood and low salinity #2 water flood, respectively, which shows significant increase to more water-wet state in large pore corners by lower salinity water flood through pore-corner filling mechanism and stripping out adsorbed crude oil from pore surface.

#### CONCLUSION

The NMR investigation has identified a mixed wetting state signature from  $T_2$  relaxation time distributions at residual oil saturation after three different salinity water floods. In each case, a higher  $T_2$  peak relaxation time than that of the bulk crude oil and fully water saturated core plug was observed.

There are two pore filling mechanisms for low salinity waterflood EOR, i.e., a porecentre filling mechanism and a pore-corner filling mechanism. The invading low salinity water displaces oil from pore-centres and from pore-corners, and strips out adsorbed oil from pore surfaces and therefore changes wettability to an increased water wet condition. Comparing oil saturation reduction and wettability index modification to increased water wet state of low salinity water flood, the contribution due to low salinity water invasion through pore-corners is much more significant than the contribution due to low salinity water invasion through pore-centres.

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Figure 1 shows the  $T_2$  relaxation time distributions of core plugs No. 156 and 157 at 100% water saturation.



Figure 3 shows T<sub>2</sub> relaxation time distributions for a bulk crude oil and for core plug No. 157 at different fluid saturation conditions;



Figure 2 shows the  $T_2$  relaxation time distributions for a bulk crude oil and for a core plug (No. 156) at different fluid saturation conditions.



Figure 4 shows the T<sub>2</sub> relaxation time distributions of sister core plugs after water flooding with three different salinity brines.