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Effects of OBM Invasion on Irreducible Water Saturation: Mechanisms and Modifications of NMR Interpretation

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Abstract

In this study, the effects of synthetic oil base mud (OBM) surfactants (emulsifiers and oil-wetting agents) on wettability alteration, NMR response and irreducible water saturation (S_{wir}) were systematically examined with Berea and limestone cores. Results show that the originally strongly water-wet Berea and limestone cores are altered to be intermediate-wet or oil-wet by OBM surfactants. As a result, S_{wir} from NMR $T_{2,\ cutoff}$ model with the default assumption of water-wetness generally underestimates the measured value. The magnitude of underestimation depends on three parameters: the type of OBM surfactants, their concentration in the flushing fluid, and the flushing volume. The magnitude of underestimation correlates with the Amott-Harvey wettability index. These results suggest that the effects of OBM invasion on estimation of S_{wir} can be minimized by controlling the volume of OBM invasion and the concentration of OBM surfactants.

The mechanisms of S_{wir} underestimation and modifications of NMR interpretation when wettability alteration occurs were investigated. In the case of an oil-bearing zone at irreducible water saturation, OBM invasion does not significantly decrease the actual S_{wir}, but changes the water and oil relaxation time distributions due to wettability alteration. This is visualized by the diffusion editing technique. When wettability alteration occurs (water-wet to intermediate-wet or oil-wet), a $T_{2,\ cutoff}$ value larger than the one based on water-wetness is needed because the irreducible water relaxes at a longer relaxation time. Correlation between this modified $T_{2,\ cutoff}$ value and the Amott-Harvey wettability index was found.

Introduction

Oil base drilling muds have the advantage of higher drilling rate and better well bore stability[1]. They are often used in zones such as problem shale or deep, hot hole, which could not be drilled safely or efficiently with a water base mud[2]. Among their additives, primary and secondary emulsifiers are used to make water emulsified in the external oil phase, and oil wetting agents are used to make the drilled cuttings and density control particles oil-wet. Excess amount of emulsifiers and oil wetting agents is often added to maintain the stability and rheological properties of the mud system[2,3]. These emulsifiers and oil wetting agents are mainly the wettability alteration materials[4] . Potentially, these OBM surfactants may invade into the near well bore formation with the base oil and change the originally preferential water-wet mineral surface to mix-wet or preferential oil-wet[5,6], especially during the spurt-loss period before the mud cake fully builds up. It was reported that OBM invasion altered the reservoir rock and affected formation evaluation from NMR well logging and special core analysis[6-8]. However, quantitative connection between the effects of OBM invasion on NMR derived parameters (S_{wir} and permeability) and some independent wettability measurements has not been investigated.

The objectives of this study are to investigate the quantitative wettability alteration by synthetic OBM surfactants, the effects of wettability alteration on NMR estimated S_{wir}, and the modifications of NMR interpretation when wettability alteration occurs. Four typical OBM surfactant systems from the industry were used. A series of concentration of emulsifiers and oil-wetting agents in the base oil and different invasion volume were examined. It aims to provide some laboratory experimental results to help to minimize the NMR misinterpretation caused by the invasion of OBM drilling fluids.

Experiments

Materials. The Berea sandstones and Texas Cream limestones studied are 1′ diameter by 1′ length. They were cored from large outcrop slabs. The Berea cores are very similar to each other with porosity of 0.17-0.19 and air permeability of 81-147 md. The limestones are also very similar to each other with porosity of 0.23-0.25 and air permeability of 6-10 md. Four systems of OBM surfactants (emulsifiers and oil-wetting agents) from the industry were used: VERSA, LLD, BOO and NOVA. The OBM invasion fluid was simulated by mixing a specified amount of emulsifiers and oil-wetting agents with base oil and aging in an oven at 75 °C for 18 hours. The ratio among the emulsifiers and oil-wetting agents was based on their amount used in the whole mud. Base oil SB (2.7 cp) is a mixture of internal olefins with C_{16} to C_{18}. The crude oil used is a North-Sea crude oil (29.2 API, 15 cp). The brine is 5% wt sodium chlorite.

Saturation Preparation and Experimental Procedures. The Berea and limestone cores were brine saturated as follows. The dry core was evacuated for 8 hours by a vacuum pump. Brine was introduced into the vacuum vessel and the core remained immersed in brine for 8 hours under vacuum. Then the core was placed in a bottle of brine with a loosely fitting rubber stopper and pressurized at 1000 psi for 8 hours.

The brine saturation was reduced to irreducible water saturation by centrifugation with air, base oil or crude oil in an L5-50P model centrifuge. The centrifuge speed corresponded to a capillary pressure of 100 psi. The centrifugation duration was 16 hours with an additional hour after the sample was turned upside down.

The cores at irreducible water saturation with crude oil or base oil were flushed with 1, 3, 5, 7, 10 or 15 PV OBM flushing fluid at a rate of 9 ml/hour in a Hassler core holder. The flushing fluids are base oil plus OBM surfactants at different concentrations (0%, 0.5%, 1%, 2% and 3%, wt %).

Amott-Harvey Wettability Index Measurements. Amott-Harvey wettability index measurements follow the flushing process. In the following, "imbibition" means water displacing oil and "drainage" means oil displacing water. For the Amott water index, the flushed core was immersed in brine in a standard imbibition cell for at least 48 hours, and the volume of oil displaced by spontaneous imbibition of brine (V_{SI}) was recorded. Then the core was centrifuged under brine with a capillary pressure of -25 psi, and the volume of oil displaced by forced imbibition of brine (V_{FI}) was recorded. The Amott water index was calculated as follows:

$$\delta_w = V_{SI} / (V_{SI} + V_{FI}) \qquad \text{………………………… (1)}$$

After the Amott water index measurement, the Amott oil index was similarly measured:

$$\delta_O = V_{SD} / (V_{SD} + V_{FD}) \qquad \text{…………… …………... (2)}$$

Where V_{SD} is the volume of water displaced by spontaneous drainage of oil after at least 48 hours, V_{FD} is the volume of water displaced by forced drainage of oil by centrifuging with a capillary pressure of 100 psi. The Amott-Harvey index was then calculated as follows:

$$I_{AH} = \delta_w - \delta_O \qquad \text{…………………………. (3)}$$

***T_2* Relaxation Time and Diffusion Editing Measurements.** NMR T_2 relaxation time at each saturation stage and diffusion editing measurements at some selected stages were made at room temperature with a Maran-2 spectrometer (Resonance, Inc.). The sample was left in the spectrometer for 15 minutes with a cover on the top of the probe to reach temperature equilibrium before NMR measurements. T_2 was measured by the CPMG pulse sequence with a short echo spacing (0.32 ms) to minimize relaxation due to diffusion. The signal to noise ratio (SNR) of all the T_2 measurements was set to be 100. A non-negative non-linear least square inversion method developed in our laboratory was used to estimate the multi-exponential T_2 relaxation time distributions[9]. Diffusion editing[10,11] measurements were carried out at 9 diffusion lengths. 3000 echoes with echo spacing of 400 μs and 400 scans were collected at each diffusion length.

Results and Discussion

Wettability Alteration by OBM Surfactants. Fig. 1 shows the Amott-Harvey wettability indices of Berea cores after flushing. When there are no OBM surfactants in the flushing fluid, the Amott-Harvey indices are close to +1. It means that the Berea cores are originally strongly water-wet. However, for all the four OBM surfactant systems, when their concentrations in the flushing fluid are as low as 0.5%, the strongly water-wet Berea cores are altered to be intermediate-wet. With the increase of concentration, the Berea cores are altered to be intermediate-wet for VERSA, slightly oil-wet for LLD, but more oil-wet for BOO and NOVA. Explanation of the different behaviors among these OBM surfactant systems is not clear yet due to lack of detailed information of their structures.

Fig. 2 shows the Amott-Harvey wettability indices of limestone cores after flushing. Similar to the Berea cores, the limestone cores are originally strongly water-wet. The limestone cores are altered to be slightly oil-wet by 1% NOVA, but strongly oil-wet by 0.5% BOO. **Table 1** lists the values of the Amott-Harvey indices for both Berea and limestone cores.

Our earlier papers[11-13] demonstrated that the separation of water and oil relaxation time distributions by the diffusion editing technique is a great help to study wettability alteration. The visualization by diffusion editing of the wettability alteration of Berea cores due to OBM surfactants was shown in the earlier paper[12]. **Fig. 3** shows the similar visualization for the limestone cores. For the water-wet sample after flushing (L15, **Table 1**), after forced brine imbibition water relaxes very close to that of 100% S_w (at strongly water-wet condition), and most of the oil relaxes at its bulk relaxation time. It means that almost all the surface is still covered by water, shielding the oil from any surface relaxation contribution. As a comparison, for the oil-wet sample after flushing (L2, **Table 1**), after forced brine imbibition, water relaxes at relaxation times longer than that of 100% S_w (at strongly water-wet condition), and almost all the oil relaxes at relaxation times shorter than its bulk value. It means that some of the mineral surface is now contacted by oil. These fluid distributions derived from the diffusion editing maps are in good agreement with the wettability conditions.

Effects of Wettability Alteration by OBM Surfactants on NMR Estimated S_{wir}. Qualitatively, wettability alteration changes the relaxation time distributions of water and oil in the pore space[12]. Therefore, S_{wir} from NMR interpretation may be affected if the wettability alteration is not noticed. This section will first address the methodology of estimating S_{wir} from NMR interpretation, and then show the quantitative effects of OBM surfactant concentration and flushing volume, and finally correlate with Amott-Harvey wettability indices.

Estimation of S_{wir} from NMR Interpretation. In the literature, $T_{2,\ cutoff}$ and spectral BVI models[14,15] were developed for estimation of S_{wir} from NMR. Because this study focuses on the effects of wettability alteration on S_{wir} and also for simplicity, the traditional $T_{2,\ cutoff}$ model was used. The default $T_{2,\ cutoff}$ values for sandstones and carbonates are 33 ms and 92 ms, respectively. For the water-wet Berea cores in this study, T_2,

$_{cutoff}$ was determined to be (32.6 ± 3.4) ms, very close to the default value of 33 ms. **Fig. 4** shows the cross-plot of S_{wir} by weighing (air/brine) and from $T_{2, cutoff}$ of 33 ms (100% S_w). They correlate very well. $T_{2, cutoff}$ of 33 ms was then used to estimate S_{wir} after flushing for the Berea cores.

Fig. 5 shows an example of the normalized incremental and cumulative T_2 distributions of Berea cores at 100% S_w, S_{wir} with air, S_{wir} with crude oil and after flushing (core B30: 10 PV SB; core B66: 10 PV (SB+3% BOO)). It shows that for core B30 which remains strongly water-wet after flushing (**Table 1**), $T_{2, cutoff}$ of 33 gives a good estimation of S_{wir} after flushing. As a comparison, for core B66 which is altered to be oil-wet after flushing (**Table 1**), the same $T_{2, cutoff}$ of 33 ms underestimates the measured value of S_{wir} after flushing. **Fig. 5** also shows that for the Berea cores at S_{wir} with crude oil, $T_{2, cutoff}$ of 33 ms overestimates the measured value of $S_{wir.}$ This is because the relaxation time of bulk crude oil interferes with that of the irreducible water (**Fig. 6**). The magnitude of overestimation for all the Berea cores studied is (0.078 ± 0.018) PV.

For the limestone cores, **Fig. 7** shows an example of the normalized incremental and cumulative T_2 distributions at 100% S_w, S_{wir} with SB and after flushing (core L15, 10 PV SB, core L59: 10 PV (SB+3% BOO)). For each limestone core, the $T_{2, cutoff}$ value was determined to be the T_2 value at which the cumulative intensity of the relaxation time distribution at SB/brine equals to the measured value of $S_{wir.}$ For the water-wet limestone cores in this study, $T_{2, cutoff}$ is (34.4 ± 3.3) ms. Similarly to the case of Berea cores, the $T_{2, cutoff}$ determined by this way gives a good estimation of S_{wir} after flushing if the core is still water-wet (L15, **Fig. 7**), but underestimates the measured value of S_{wir} if the core is altered from water-wet to oil-wet (L59, **Fig. 7**).

Effects of OBM surfactants concentration. **Fig. 8** shows an example of the measured and estimated values of S_{wir} for Berea cores flushed with OBM surfactant system BOO at different concentrations. When the concentration of BOO in the flushing fluid increases, S_{wir} was more severely underestimated. For the four OBM systems studied, similar trend was found (**Fig. 9**: Berea, **Fig. 10**: limestone). For Berea cores, **Fig. 9** shows that the magnitude of S_{wir} underestimation (defined as S_{wir}, weighing - S_{wir}, $T_{2, cutoff}$) generally increases with the concentration of OBM surfactants in the flushing fluid. Among the four OBM surfactant systems, NOVA and BOO underestimate the S_{wir} more seriously than VERSA, with LLD in between. These differences are consistent with the Amott-Harvey wettability indices as discussed later in this paper. **Fig. 10** shows the similar trend for limestone cores with NOVA and BOO.

Effects of flushing volume. The effects of flushing volume on S_{wir} estimation was investigated using (SB+3% BOO) for both Berea and limestone cores. **Fig. 11** shows that the estimated S_{wir} starts to obviously deviate from the measured value after about 3 PV flushing, and it reaches a plateau after about 7 PV flushing. It suggests that the fluid loss control in the drilling process may be a key factor in minimizing the NMR misinterpretation due to OBM invasion.

Correlation of S_{wir} underestimation with Amott-Harvey indices. **Fig 12** shows the correlation between the magnitude of underestimated S_{wir} and the corresponding Amott-Harvey index. Here the four OBM surfactant systems were not differentiated. For the Berea cores, in the intermediate-wet to oil-wet region, the magnitude of underestimation increases linearly with the decrease of the Amott-Harvey index (R^2 = 0.80). When extrapolated to Amott-Harvey index of -1, which corresponds to strongly oil-wet condition, the magnitude of underestimation is about 0.128. This value is reasonable in the sense that it is smaller than S_{wir} measured from weighing ((0.219 ± 0.006) PV for all the cores studied). It suggests that even when the core has been altered to be strongly oil-wet, there is still some water remaining in the small pores. As expected, in the water-wet region, there is no underestimation. It is similar for the limestone cores. But no correlation line was drawn for the limestone cores due to insufficient data points.

Table 1 summarizes the measured and estimated values of S_{wir} for all the cores for which the Amott-Harvey wettability index measurements were performed.

Mechanism of S_{wir} Underestimation and Modifications of NMR Interpretation when wettability alteration occurs. The above sections show that S_{wir} is underestimated when wettability alteration occurs. But how much of the underestimation is due to the actual change of S_{wir} (physically flushed out of the pore space or emulsification of water in the flushing fluid by surfactants)? This question was examined by the quantitative Karl-Fisher analysis of the amount of water in the flushing effluents. **Fig. 13** shows the amount of water in the flushing effluent, as well as the measured and estimated S_{wir} after flushing for B31 (flushed with 10 PV SB), B26 (flushed with 10 PV (SB+3% NOVA) and B66 (flushed with 10 PV (SB+3% BOO). It shows that the amount of water in the flushing effluent is relatively small compared with the total amount of S_{wir} underestimation. It means that the actual S_{wir} does not change much due to wettability alteration.

The diffusion editing maps give a good visualization of the mechanism of S_{wir} underestimation due to wettability alteration. **Fig. 14** shows the diffusion editing maps of B77 at 100% S_w and after flushing, together with the $T_{2, cutoff}$ value determined assuming water-wetness (vertical line). For 100% S_w at strongly water-wet condition, by definition the irreducible water relaxes below the $T_{2, cutoff}$. B77 was altered to oil-wet after flushing (**Table 1**). As a result, the corresponding diffusion editing map shows that some of the irreducible water now relaxes above the $T_{2, cutoff}$ value, and the amount of water relaxing below the $T_{2, cutoff}$ decreases quite a lot. If the wettability alteration is not noticed and the same $T_{2, cutoff}$ as for water-wet condition is used, S_{wir} will be underestimated.

The mechanism of S_{wir} underestimation illustrated above confirms that a larger value of $T_{2, cutoff}$ should be used when wettability alteration occurs. **Fig. 15** quantitatively shows that for both Berea and limestone, the larger the magnitude of S_{wir} underestimation, the larger the modified $T_{2, cutoff}$ value should be.

Finally, **Fig. 16** shows the correlation between the modified values of $T_{2, cutoff}$ versus the Amott-Harvey index. For the Berea cores from intermediate-wet to oil-wet, they correlate well with each other (R^2 = 0.69). Similar correlation will be developed for limestone cores after more data points are acquired (future work). As expected, at the water-wet region, there is no need for modification.

Discussions. The lowest concentration of the OBM surfactants in the flushing fluid examined in this study was 0.5% wt. This value could be still larger than that in the field filtrate. The implications of this study are that if in the field the formation wettability is altered to be only intermediate-wet, then the S_{wir} will not be severely underestimated. However, wettability alteration to oil-wet will underestimate S_{wir}.

Our future work is to examine lower OBM surfactants concentration and the effect of aging.

Conclusions

Under the experimental conditions of this study, the strongly water-wet Berea and limestone cores are altered to be intermediate-wet or oil-wet by the OBM surfactants. As a result, S_{wir} from the $T_{2,\ cutoff}$ model assuming water-wetness in cases where wettability alteration occurs generally underestimates the measured value of S_{wir}. This effect depends on the type of OBM surfactant systems, their concentration, and the flushing volume. The magnitude of underestimation correlates with the Amott-Harvey index.

In the case of a Berea or limestone core at irreducible water saturation with crude oil or base oil, OBM surfactants invasion does not significantly decrease the actual S_{wir}, but increases the relaxation time of some of the irreducible water to be above the $T_{2,\ cutoff}$ value as determined at water-wet condition. The visualization of this relaxation time increase by the diffusion editing maps confirms that a larger value of $T_{2,\ cutoff}$ can be used to get the correct S_{wir} in cases of wettability alteration from water-wet to intermediate-wet or oil-wet. The modified values of $T_{2,\ cutoff}$ correlate with both the magnitude of S_{wir} underestimation and the Amott-Harvey index.

Results of this study suggest that in the real drilling process, the effects of OBM invasion on NMR misinterpretation when wettability alteration occurs can be minimized by controlling the invasion volume and the concentrations of OBM surfactants in the invasion fluid.

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Nomenclature

δ_O = Amott oil wettability index
δ_w = Amott water wettability index
I_{AH} = Amott-Harvey wettability index
SNR = signal to noise ratio in T_2 measurements
S_w = water saturation, fraction
S_{wir} = irreducible water saturation, fraction
T_2 = transverse relaxation time, ms
$T_{2,\ cutoff}$ = cutoff value of T_2 to estimate S_{wir} from NMR, ms
V_{FI} = volume of oil displaced by forced brine imbibition, ml
V_{SI} = volume of oil displaced by spontaneous brine imbibition, ml
V_{FD} = volume of water displaced by forced oil drainage, ml
V_{SD} = volume of water displaced by spontaneous oil drainage, ml

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Table 1 Amott-Harvey wettability indices, measured and estimated S_{wir} and modified $T_{2,\ cutoff}$

Core #[a]	Surf. Sys.	Conc. (wt %)	I_{AH}	S_{wir}, meas. (PV)	S_{wir}, $T_{2,cutoff}$ (PV)	$T_{2,cutoff}$ modif. (ms)
B44 [b]	-	-	0.93	-	-	-
B27	-	0%	0.95	0.220	0.214	44.8
B30	-	0%	0.92	0.211	0.204	33.0
B72	-	0%	0.93	0.215	0.204	34.5
L15	-	0%	0.89	0.171	0.182	28.6
B56	VERSA	0.5%	0.08	0.215	0.203	45.6
B57	VERSA	1%	0.05	0.219	0.199	50.2
B107	VERSA	2%	0.03	0.218	0.189	64.8
B32	LLD	0.5%	-	-	-	48.3
B28	LLD	1%	-0.10	0.223	0.197	50.1
B34	LLD	2%	-0.35	0.217	0.177	67.1
B16	BOO	0.5%	-0.12	0.216	0.195	42.3
B45	BOO	1%	-0.38	0.221	0.172	77.5
B58	BOO	2%	-0.52	0.223	0.143	110.8
B66	BOO	3%	-0.51	0.215	0.131	88.3
B91	BOO	3%	-0.50	0.230	0.134	106.1
B26	NOVA	3%	-0.57	0.233	0.121	118.2
B77	NOVA	3%	-0.59	0.212	0.127	97.5
B80 [c]	NOVA	3%	-0.68	0.211	0.136	82.6
B40 [c]	NOVA	3%	-0.66	0.218	0.142	89.2
L7	NOVA	1%	-0.38	0.165	0.130	51.1
L13	NOVA	2%	-	0.180	0.113	71.1
L2	NOVA	3%	-0.53	0.175	0.102	96.2
L16	BOO	0.5%	-0.86	0.166	0.118	56.8
L35	BOO	1%	-0.88	0.174	0.101	76.9
L36	BOO	2%	-0.89	0.166	0.102	79.5
L59	BOO	3%	-0.90	0.171	0.089	133.2
L8	BOO	3%	-0.90	0.185	0.108	83.2

[a]: "B" stands for Berea and "L" stands for limestone
[b]: No flushing before Amott-Harvey measurement
[c]: Flushing volume 15 PV, 10 PV for other cores

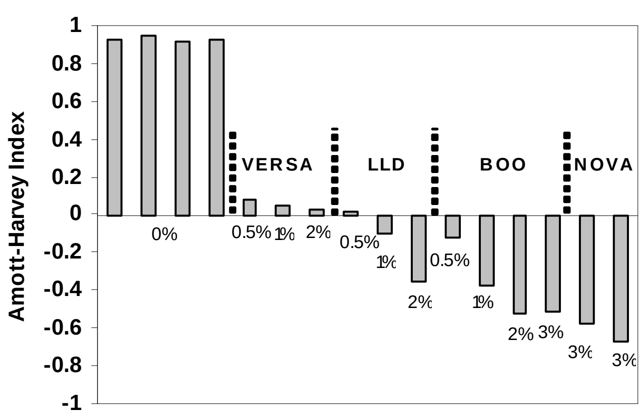

Fig. 1 Amott-Harvey indices of Berea cores after flushing

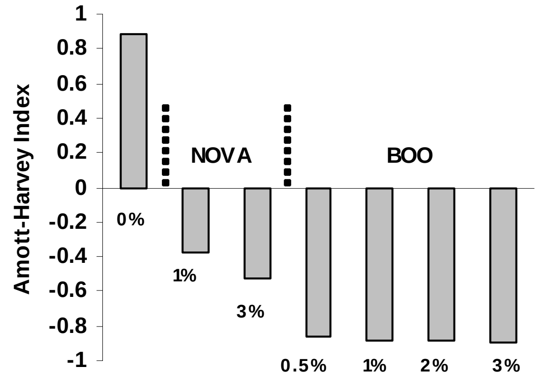

Fig. 2 Amott-Harvey indices of limestone cores after flushing

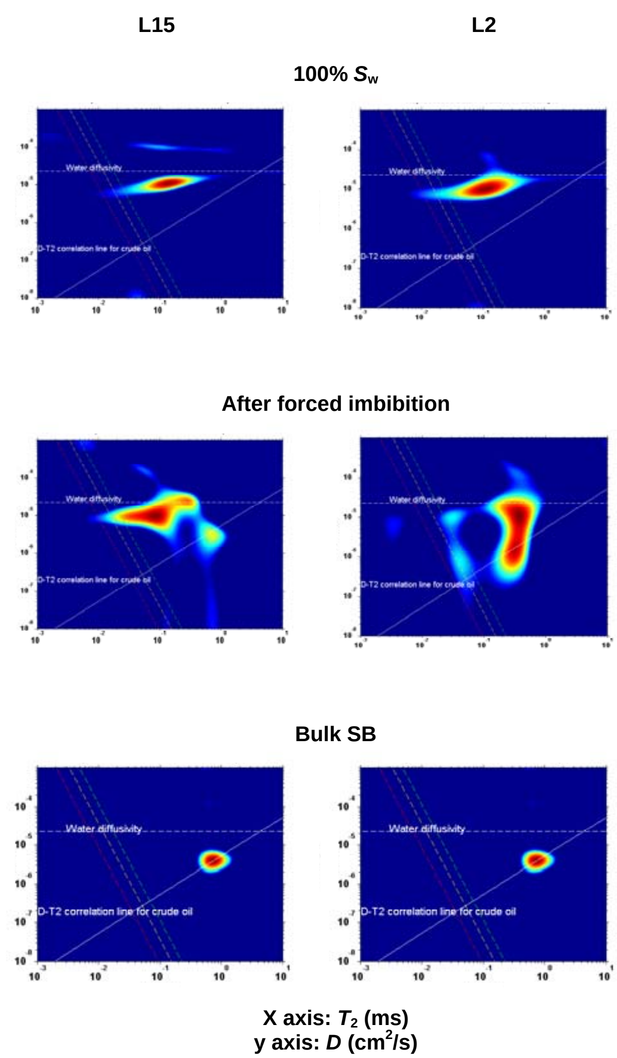

Fig. 3 Diffusion editing maps of 100% S_w, after forced imbibition and bulk SB for Limestone L15 (left, water-wet after flushing) and L2 (right, oil-wet after flushing)

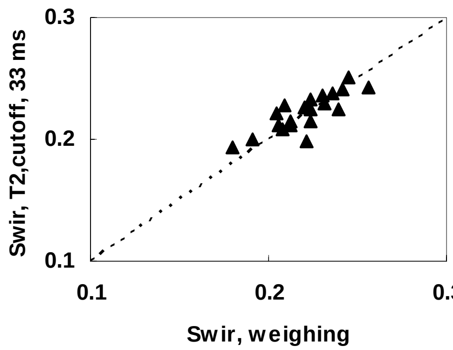

Fig. 4 Cross-plot of S_{wir} by weighing and from $T_{2,\ cutoff}$ of 33 ms for 100% S_w of Berea cores.

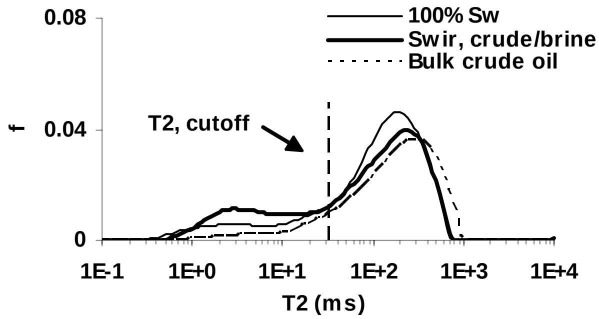

Fig. 6 Interfere of relaxation time of bulk crude oil with that of irreducible water (Berea core B30).

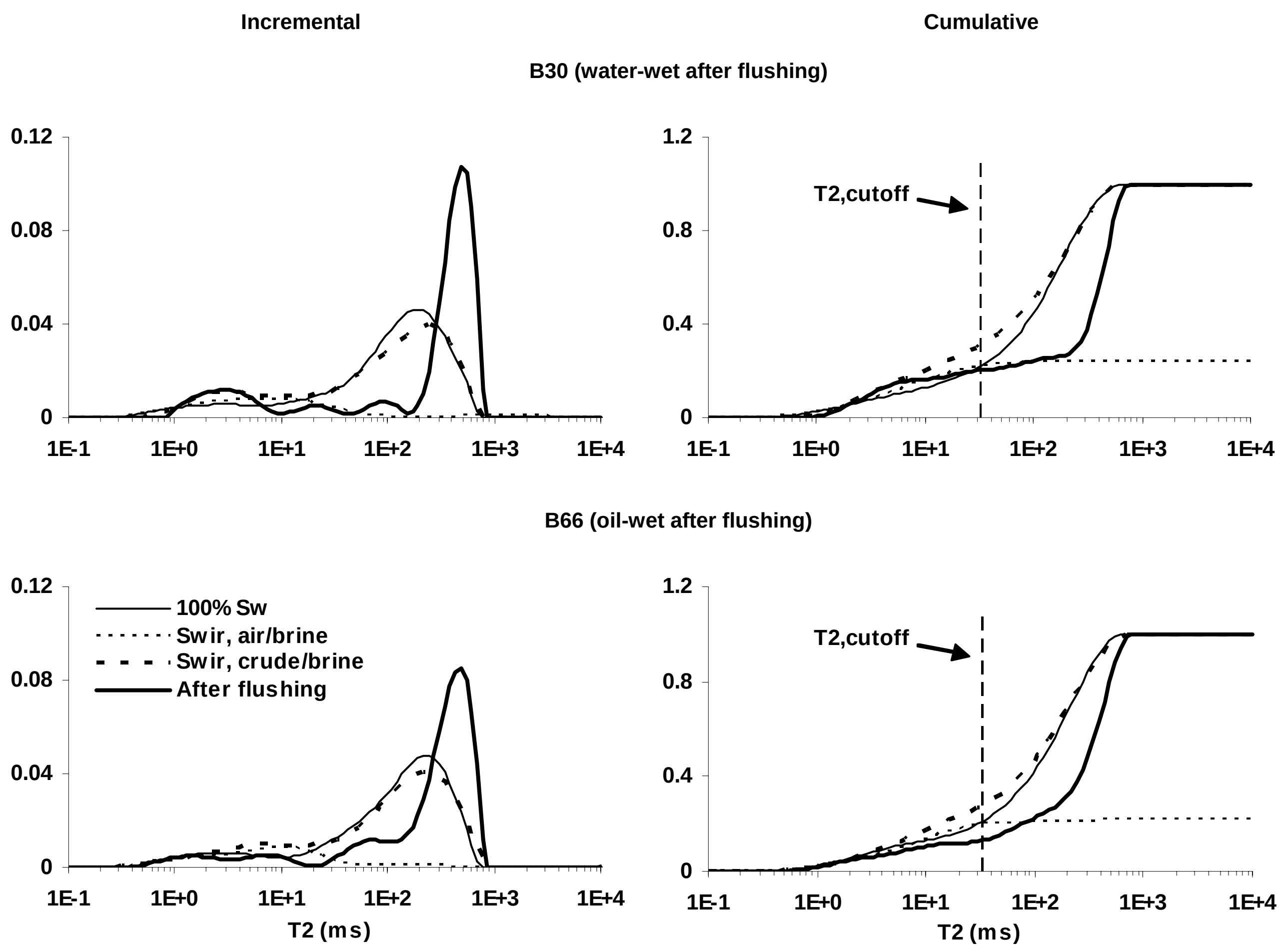

Fig. 5 Incremental and cumulative T_2 distributions for Berea B30 and B66 at 100% S_w, S_{wir} with air, S_{wir} with crude oil and after flushing.

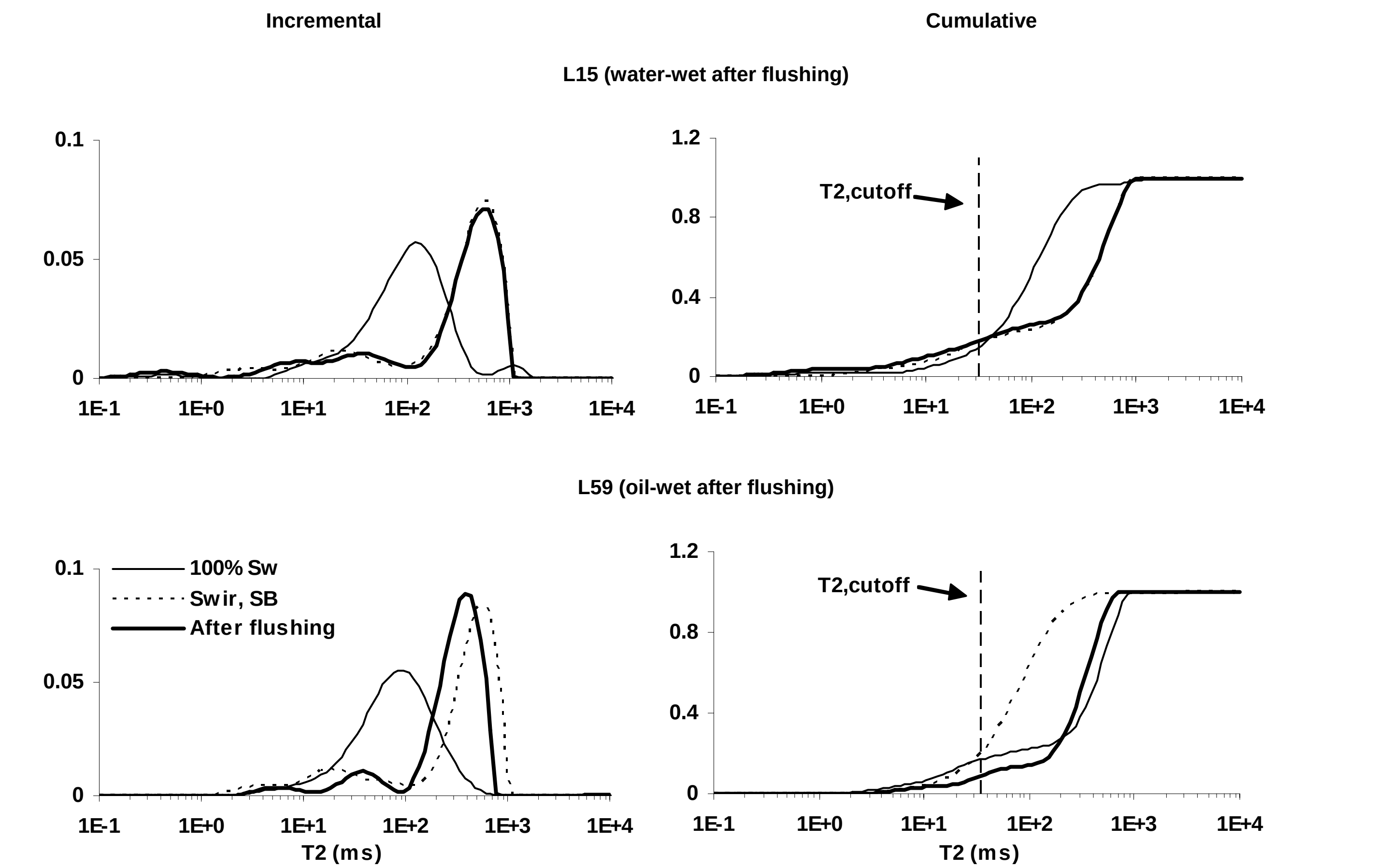

Fig. 7 Incremental and cumulative T_2 distributions for limestone L15 and L59 at 100% S_w, S_{wir} with SB and after flushing.

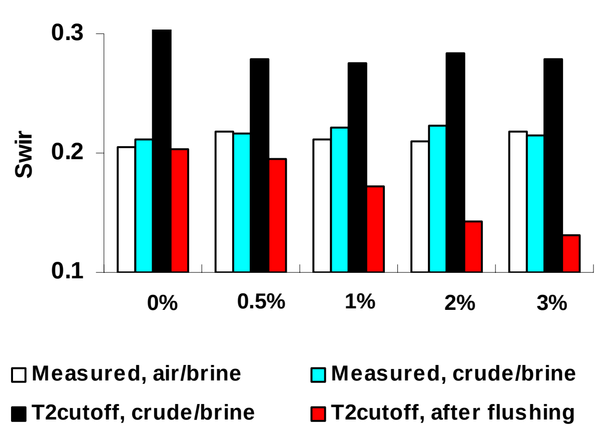

Fig. 8 S_{wir} measured by weighing and estimated from $T_{2,\ cutoff}$ of 33 ms (Berea cores, OBM surfactant system: BOO)

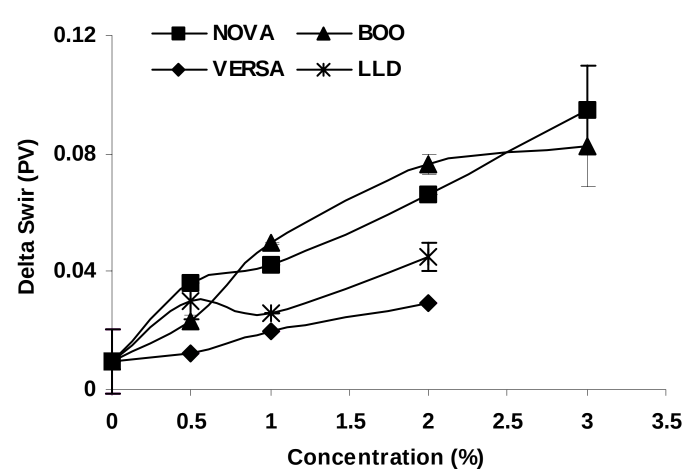

Fig. 9 Magnitude of S_{wir} underestimation with respect to the OBM surfactants concentration in the flushing fluid (Berea cores).

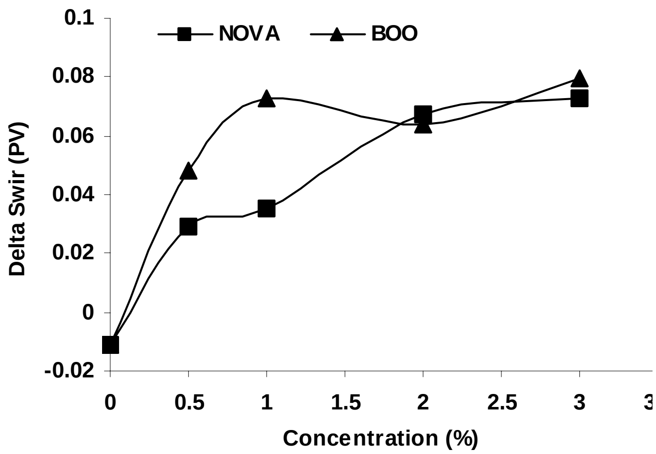

Fig. 10 Magnitude of S_{wir} underestimation with respect to the OBM surfactants concentration in the flushing fluid (limestone cores).

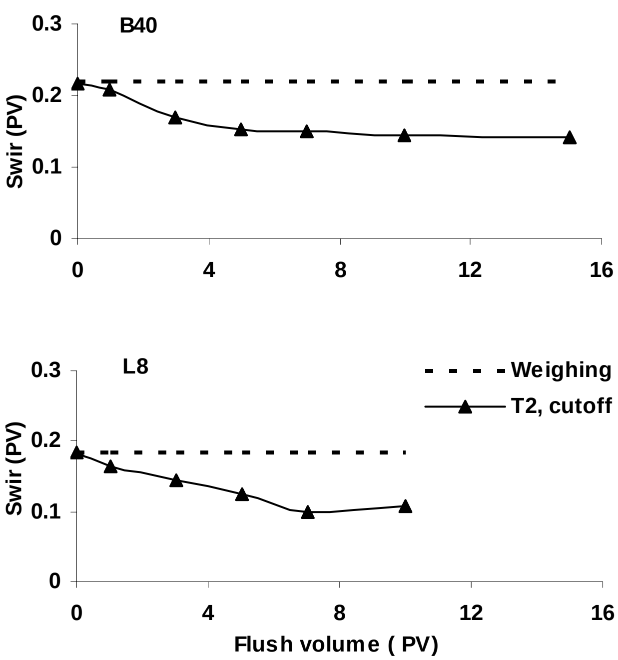

Fig. 11 Effects of flush volume on S_{wir} underestimation for Berea B40 (top) and limestone L8 (bottom)

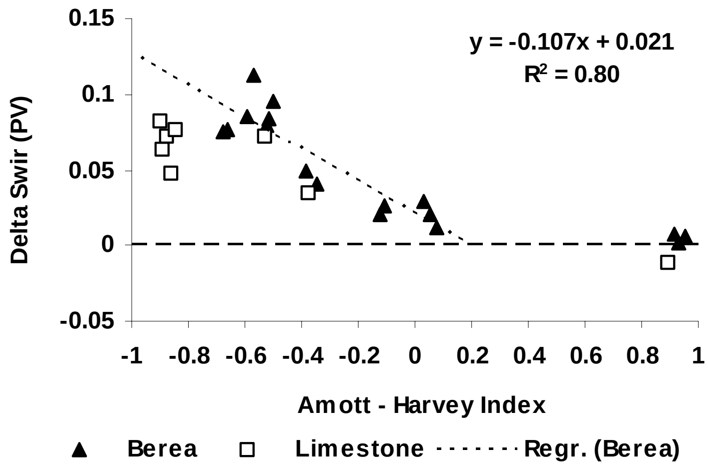

Fig. 12 Magnitude of S_{wir} underestimation versus Amott-Harvey index

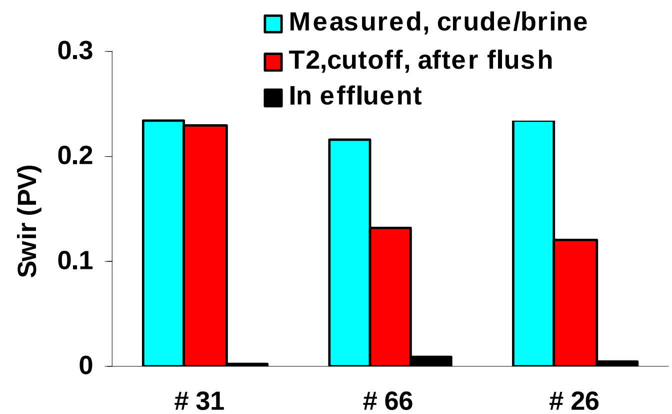

Fig. 13 Karl-Fisher analysis of water amount in the flushing effluents.

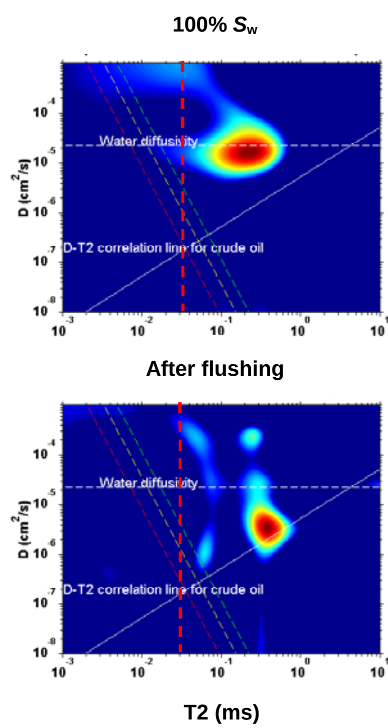

Fig. 14 Diffusion editing maps of 100% S_w and after flushing for Berea core B77 (red dashed line: $T_{2,\,cutoff}$ of 33 ms).

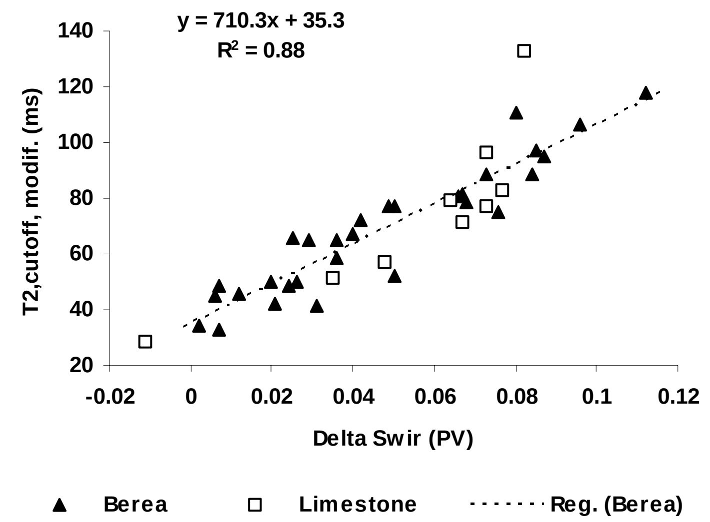

Fig. 15 Modification of $T_{2,\ cutoff}$ versus magnitude of S_{wir} underestimation.

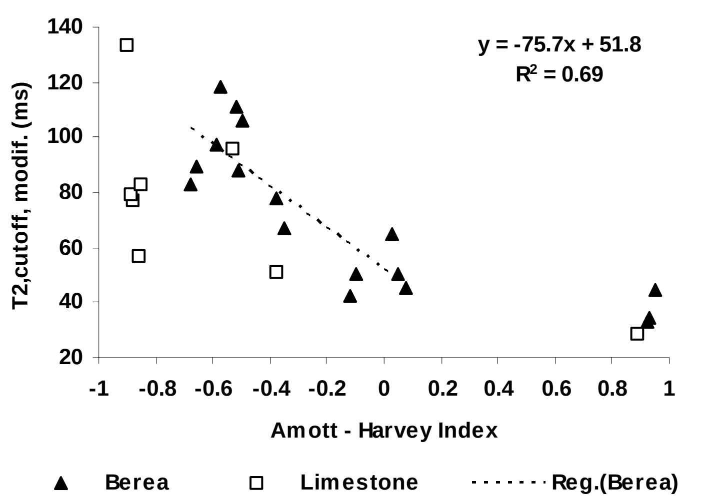

Fig. 16 Modification of $T_{2,\ cutoff}$ versus Amott-Harvey wettability index.