Core cleaning and wettability restoration – selecting appropriate method

Raheleh **Farokhpoor[1], *Lars* Sundal[1], *Anne* Skjærstein[1], *Albert* Hebing[2], *Xiangmin* Zhang[2], and *Lucian* Pirlea[2]**
[1]Lundin-Energy, Norway, [2]PanTerra Geoconsultants, The Netherlands

Abstract. The core cleaning approaches aim to remove native crude oil, mud filtrates and evaporated salts which leads to strongly water-wet cores. In the standard core cleaning method, the solvent(s) injection continues until no more oil is observed in effluent. This is generally confirmed by visual examination, rather than by analyzing the composition of effluent, simply because it is expensive.

In this work, we selected two preserved rock sections from an oil reservoir in North Sea. 1.5-inch diameter core plugs were cleaned by two different flush cleaning programs (so-called Program-1 and 2). In Program-1, samples were flushed first with 75% toluene + 25% methanol and then followed by alternate of toluene-chloroform-methanol until the samples were deemed cleaned from visual examination. In Program-2, samples were flushed by alternating toluene-tetrahydrofuran-chloroform for 8 cycles. Oil effluents from Program-2 were collected for composition GC analyses.

The efficiencies of two flush cleaning programs were compared by measuring the wettability of the samples by combined Amott-USBM wettability method. The USBM index shows samples after cleaning program-2 are more water wet. Samples were then aged in crude oil at reservoir conditions for 4 weeks. Drainage and imbibition capillary pressure using centrifuge and porous plate and the end-point liquid permeabilities were then measured on restored samples. End-point properties after aging process, showed wettability being restored to intermediate water-wet as is expected from field production history.

This study shows that standard cleaning does not fully clean these samples. Meanwhile, the elaborate Program-2 is often impractical, takes too long, is expensive and limited by laboratory capacity.

1. Introduction

Not every feature in core is geological! No matter how careful the attempt to collect and preserve core is, it can be affected by the process of collection, like drilling induced fractures, discoloration by drilling fluids and cutting marks.

A big challenge in SCAL analysis is restoring wettability of core material to a representative reservoir wettability. Wettability determines fluid distribution and fluid flow of wetting and non-wetting phases and is greatly affected by wettability restoration protocol. A standard protocol consists of cleaning the samples to a strong water-wet state, establishing representative initial water saturation and then, aging the samples with dead crude oil at reservoir conditions [1], [2]. The last step is believed to reproduce the core wettability to a representative reservoir state. Inadequate cleaning at the first step may results in a weak water-wet state and disrupt the final wettability state of the core.

The motivation of this present work comes from an earlier extensive SCAL study on preserved core samples from a sandstone reservoir in the Norwegian Continental Shelf (NCS). Large variations in fluid flow properties from different types of experiments was observed. Experiments included steady-state relative permeability, imbibition capillary pressure from centrifuge and porous plate and combined Amott-USBM wettability tests. These contradictory results led us to re-examine the wettability restoration procedure and ultimately the cleaning program. Cleaning is often performed using solvent in Soxhlet extraction or flushing in a core holder at controlled temperature. A typical solvent system used is combination of toluene and methanol, or chloroform or azeotropic solvents mixture to increase efficiency. But we question if this approach works equally efficient for all types of conventional oil.

In this study, the typical cleaning protocol is compared with a more effective program which tends to remove any trace of hydrocarbon in the cores and it was inspired by a relevant study performed on sandstone cores from North

Sea field [3]. This was followed by compositional analysis of effluents after each cleaning cycles. Afterwards, wettability of the clean samples was determined by Amott-USBM method to undermine the effectiveness of the two programs. Later, the most water-wet samples were aged by dead crude oil at reservoir conditions. And then, imbibition capillary pressure, endpoint saturation and relative permeabilities were measured and compared with not-aged samples.

2. Core material

Two preserved core materials (10 cm in diameter and 20 cm in length), from oil and waters zones, were selected for this study. X-ray CT is used to visualize the internal structure of whole core pieces and plugs and are shown in Figure 1. Heterogeneities, fractures, mud invasion and other factors that affect the local density will show up on a CT-image. The 35mm diameter core plug samples are drilled parallel to apparent bedding with a synthetic formation water (SFW). From preserved samples (PS), a subsample was taken for petrographic analysis (Thin section, SEM and XRD Whole Rock and Clay Fraction) and high pressure mercury injection (MICP) on cleaned and dry samples.

The samples are characterized as fine- to medium-grained subarkoses mainly containing quartz grains with abundant K-Feldspar grains. Primary porosity is moderately interconnected and authigenic illite locally fills intergranular pores. Clusters of kaolinite and mixed layer illite-smectite was also observed, see Figure 2. Whole rock and clay characterization was done by XRD analysis on end-trims and are given in Table 1. From MICP experiments, fairly similar pore throat size distribution was derived for both samples. As it can be observed in Figure 3, pore throat size is predominately unimodal with mean hydraulic radius of 11-15 µm.

Final check was to make sure the preserved cores were not damaged by drilling mud which is water-based mud in this case. A large thin section (10 x 4 cm) from a whole core was taken with the short side parallel to the core axis and the long axis parallel to bedding. High resolution images (Figure 4) shows mud particles are only present in thin layers at the outermost edges of the core and have not invaded the core deeper than 3 or 4 layers of sand-sized grains. Therefore, it was concluded the inner part of the core is unaffected by mud particle.

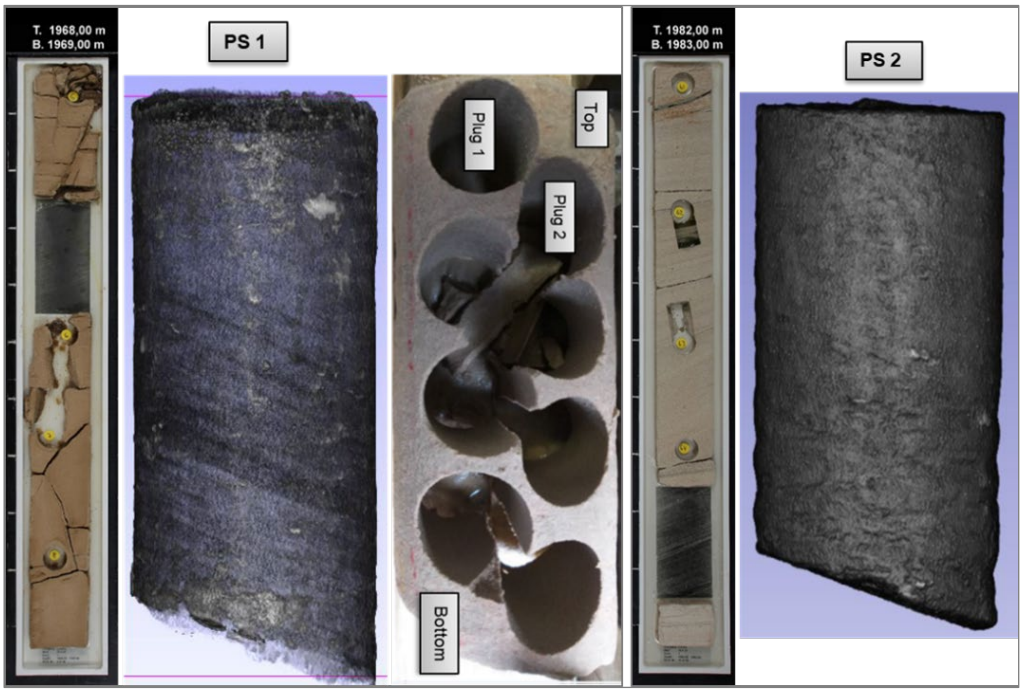

Figure 1: Photo of core section and CT scans of preserved samples (PS).

Table 1: XRD analysis of whole rock and clay fraction composition

	Whole Rock Composition (%BW)							Clay Fraction (%BW)			
Sample	Quartz	Orthoclase	Kaolinite/ Chlorite	Halite	Illite	Dolomite	Ankerite	Illite	Illite/ Smectite	Kaolinite	Chlorite
PS 1	60	32	4	tr	1	-	2	20	12	54	14
PS 2	62	28	6	1	2	1	-	10	2	88	-

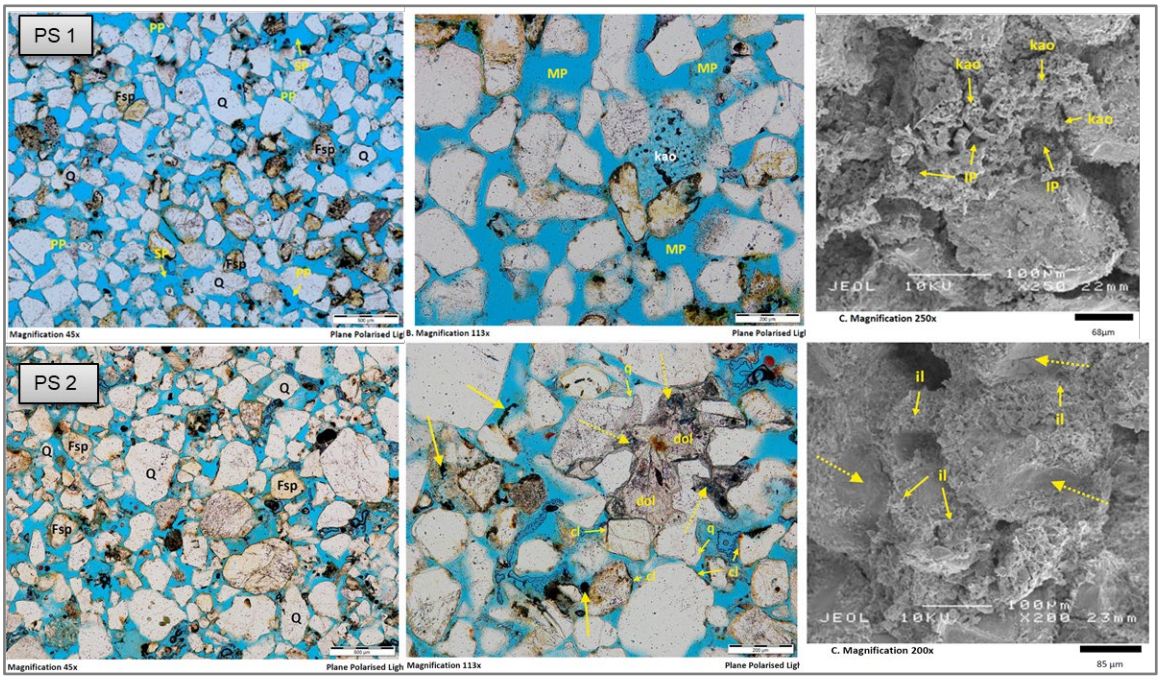

Figure 2: Images of thin section plates and SEM analysis (to the right). Grain dissolution resulted in mouldic pores (MP) and oversized pores and some places is filled by deformed kaolinite (kao) or patches of dolomite cement (dol). Grain surfaces exhibit continuous coatings illite and illite-smectite (il). Q: quartz, Fsp: feldspar, Cl: chlorite, IP: Intercrystalline pores, SP: secondary porosity.

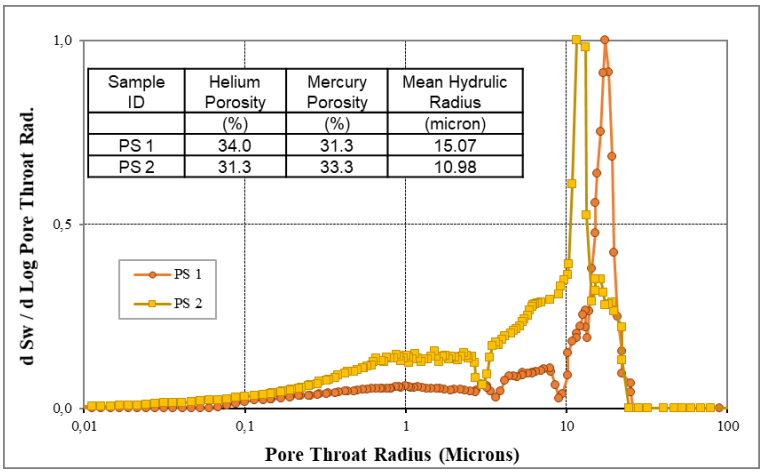

Figure 3: Pore throat size distribution from MICP experiment.

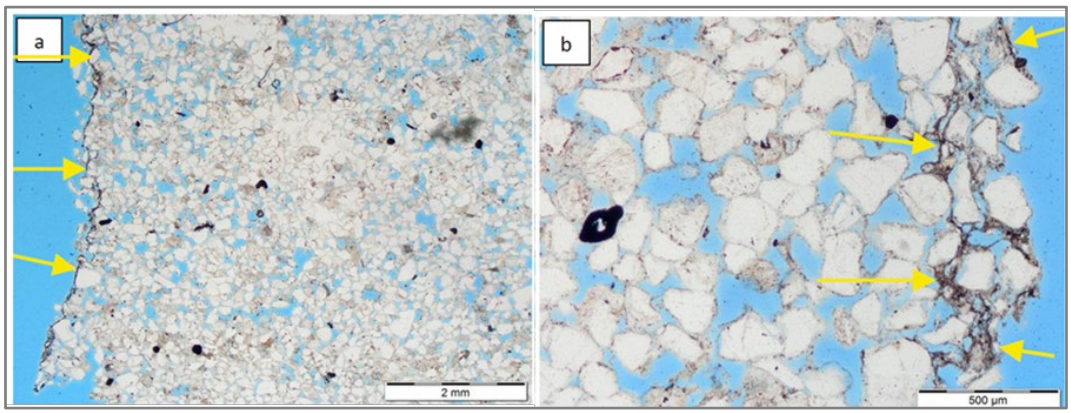

Figure 4: Thin section photomicrographs illustrating the occurrence of mud in the core sample.

3. Core cleaning

In this section the comparative cleaning results of 4 core plug samples are described. Cleaning Program-1 is a standard protocol and cleaning Program-2, is the more elaborate (aggressive) cleaning method. The flush cleaning in both Program-1 and 2 were performed at 60 °C and 20 bars confining pressure with the flow rate of 0.3 ml/min. The individual sample was jacked in a Viton sleeve and loaded into hydrostatic core holder. At controlled temperature, solvent was injected via an automated flushing cleaning system equipped with three KNAUER pumps. Program-1 and 2 are described below:

Program 1:

1. Started with low rate (0.5 ml/min) flush cleaning of mixture of 75% toluene and 25% methanol.
2. Then followed by alternate injection of toluene-chloroform-methanol until effluent was clear.
3. For each sample about 251 ml (~16 pore volumes) solvent was flushed through the sample
4. Absolute permeability to methanol in both directions was measured before samples were sent to hot oven drying and is given in Table 2.

Program 2:

1. The plugs first were flushed with two pore volumes (PV) of toluene to remove the bulk oil.
2. Flushing by 2 PV of tetrahydrofuran (THF) to remove remaining oil and water and effluent was collected (see Figure 5).
3. The oil composition in effluent was measured up to C_{42+} utilizing a high-resolution capillary gas chromatography (GC) and an FID detector.
4. Plugs were then flushed by 2 PV of chloroform to desorb THF in step 2.
5. Steps 1 to 4 were repeated for 8 cycles (~ 42 PV) and effluent after each THF flooding (a total of 8 effluents) were analyzed by GC.
6. At the end, plugs were flushed by methanol to remove polar solvents, salts and water.
7. Absolute permeability to methanol in both directions was measured before samples were sent to hot oven drying.

Table 2: petrophysical properties of core plugs

Sample	Helium Porosity	Klinkenberg Permeability	Methanol Permeability	
			Forward	backward
Number	%	(mD)	(mD)	(mD)
2 - PS 1	32.9	1644	1143	1117
4 - PS1	32.3	1374	1137	958.8
9 - PS2	31.3	1373	1102	967.4
10 - PS2	31.0	1122	632.2	600.0

During cleaning Program-2, each subsequent cleaning cycle (methanol/THF/chloroform) removed more oil. The remaining oil fractions became heavier with each flushing, as the molecular weight of crude changed from 225 g/mol at first cycle to 550 g/mol at cycle 8 (see Figure 6), which corresponds to fractions heavier than C_{42}. This is explained by the fact that the relatively light fractions are flushed first and the residual oil composition shifting towards a higher C number. This can be also noticed in the shapes of the chromatograms in Figure 7, where there is a clear reduction in lighter fraction and a shifting of the whole spectrum towards the heavy end (after the retention time of 50 on the graph).

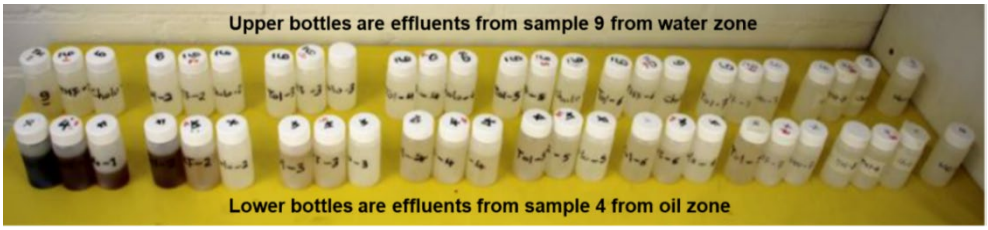

Figure 5: Effluents collected from core plugs after cleaning Program-2. Stack of three bottles representing different cycles.

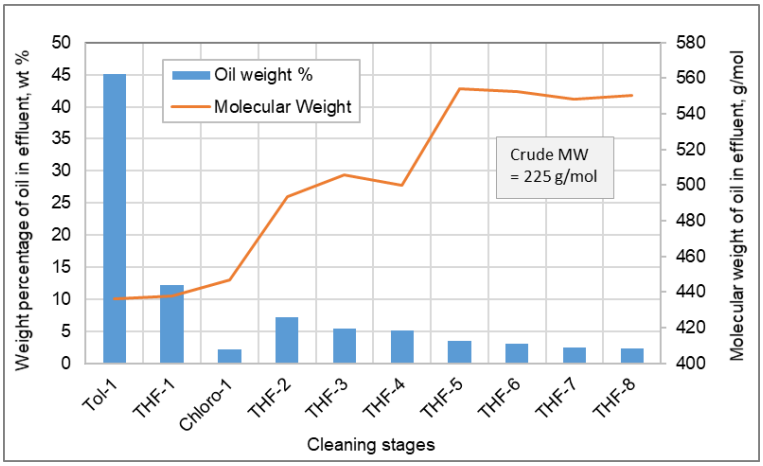

Figure 6: Evolution of oil fraction wt % and molecular weight of oil fraction during the cleaning stages.

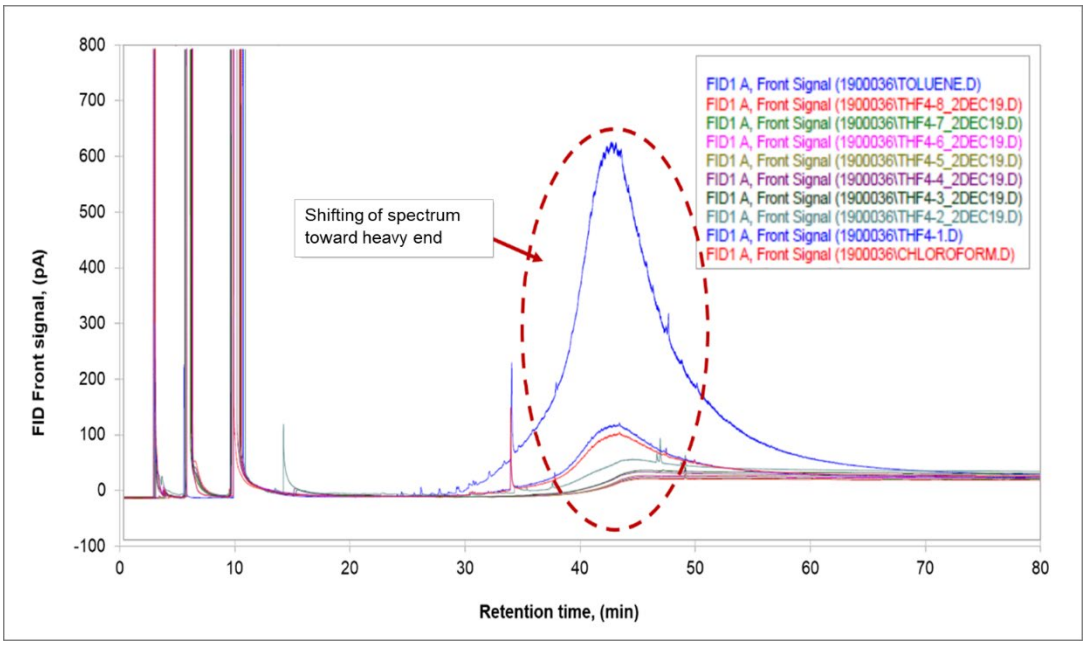

Figure 7: FID front signal over time showing overlapped chromatograms of effluents. First peak is for THF, second for Chloroform and third for toluene. The last peaks are for oil heavy component as it is shifted toward longer retention time from first effluent to eighth effluent.

4. Wettability analysis on clean cores

Two cleaned samples from each of the two different cleaning programs were used for combined Amott and USBM wettability analyses [4], [5], [6], [7]. The aim was to compare the effect of cleaning methods on wettability.

The clean and dry samples were first fully saturated with synthetic formation brine. Each sample was first placed in an Amott cell for two weeks filled with mineral oil. The target water saturations (~20-25%) was achieved by a centrifuge oil-brine drainage process. The samples were then placed in glass Amott cells filled with synthetic formation brine and spontaneous imbibition of brine was monitored before the samples were loaded into the centrifuge for forced imbibition. After establishment of S_{or}, the samples were loaded into Amott cells where spontaneous and forced imbibition of oil was measured.

Based on the same experimental data, two types of wettability indices are calculated, the USBM wettability index (W) and Amott-Harvey Index and are listed in Table 3. All four samples are water-wet based on wettability index. It was observed that water was much easier to spontaneously imbibe into samples than Soltrol oil. This is a direct indication that water is the wetting fluid. Although the Amott-Harvey index does not show much difference in wettability of the four samples, the USBM index seems to show that sample 4 and 9, cleaned by program-2, are more water wet compared to sample 2 and 10, cleaned by Program-1.

Table 3: The Amott-Harvey and USBM indexes after combined Amott-USBM Wettability test at ambient conditions

Sample Number	Amott- Harvey Index	USBM Index	Cleaning Program
2-PS 1	0.54	0.29	Program-1
4-PS 1	0.47	0.75	Program-2
9-PS 2	0.52	0.52	Program-2
10-PS 2	0.57	0.18	Program-1

Effective permeability for oil at irreducible water saturation (S_{wi}) and for water at residual oil saturation (S_{or}) were also measured. The core was mounted in a core holder with 20 bar net overburden pressure, measurements were performed at room temperature with four different flow rates. The results are summarized in Table 4. The oil permeability at irreducible water saturation (K_O @ S_{wi}) is close to the Klinkenberg permeability and significantly higher than water permeability at residual oil saturation (K_W @ S_{or}). These end-points also support that the samples are water-wet and are consistent with combined Amott-USBM wettability test.

Table 4: The end-point oil and water saturations and permeabilities

End Point data from Amott-USBM					
Sample	S_{wi}	K_W@S_{or}	S_{or}	K_O@S_{wi}	S_{wi}
Number	(frac)	(mD)	(frac)	(mD)	(frac)
2-PS 1	0.200	83.6	0.298	1116	0.217
4-PS 1	0.200	359.3	0.194	1131	0.236
9-PS 2	0.250	85.6	0.296	1135	0.289
10-PS 2	0.250	130.6	0.255	921.7	0.284

5. Capillary pressure and endpoint permeability after wettability restoration

For further investigation, four more core plugs were selected from the two preserved samples and then they were flush cleaned by Program-2. The clean and dry samples were first fully saturated with synthetic formation brine. The samples were spun in centrifuge to bring to the initial (target) water saturation (S_{wi}) by injecting crude oil. Samples were then aged in crude dead oil at reservoir conditions (80 °C and 190 bars) for 4 weeks. Properties of formation water and reservoir oil are given in Table 5. Afterwards, the crude oil in the sample was replaced first by decaline and then by Soltrol oil. Flooding the core plugs by decaline is to avoid any chemical reaction between crude oil and Soltrol. The oil permeability at initial water saturation (S_{wi}) was measured by the end of the flushing by Soltrol oil. Oil-brine drainage and imbibition capillary pressures were then measured by two different methods, multi-speed centrifuge and porous plate.

Table 5: Reservoir fluid properties

Parameter	Unit	Value
Viscosity of reservoir oil	cp	0.52
Density of stock tank oil	kg/Sm³	855
Density of reservoir oil	kg/Sm³	700
Density of formation water	kg/Sm³	1050

5.1 Capillary pressure by centrifuge:

After measurement of K_O @ S_{wi}, the samples were weighed and loaded into an ultracentrifuge in (brine) imbibition mode. The volume of displaced oil was monitored on consecutive days at each capillary pressure to ensure samples had reached stable saturations. The samples were stored for few days to allow the fluid to redistribute across the sample before measuring effective permeability for water at residual oil saturation (K_W @ S_{or}).

The samples were loaded again into an ultracentrifuge in a drainage mode where brine was displaced by mineral oil (secondary drainage process). End-face fluid saturation at each capillary pressure step was modelled with Hassler-Brunner method. Capillary pressure at the final stage of centrifuge and corresponding bound numbers for imbibition and drainage are given in Table 6. Afterwards, the effective permeability for oil at irreducible water saturation (K_O @ S_{wi}) was measured. The results are presented in Table 7 and Figure 8.

Table 6: Capillary pressure and corresponding bound number used at the last stage of multi-speed centrifuge

Sample	Imbibition		Secondary Drainage	
	End-Pc	Bound No.	End-Pc	Bound No.
Number	(Pci)	[-]	(Pci)	[-]
8 - PS 1	-62.6	-2.4E-04	50.3	1.9E-04
14 - PS 2	-62.7	-5.5E-04	50.4	4.4E-04

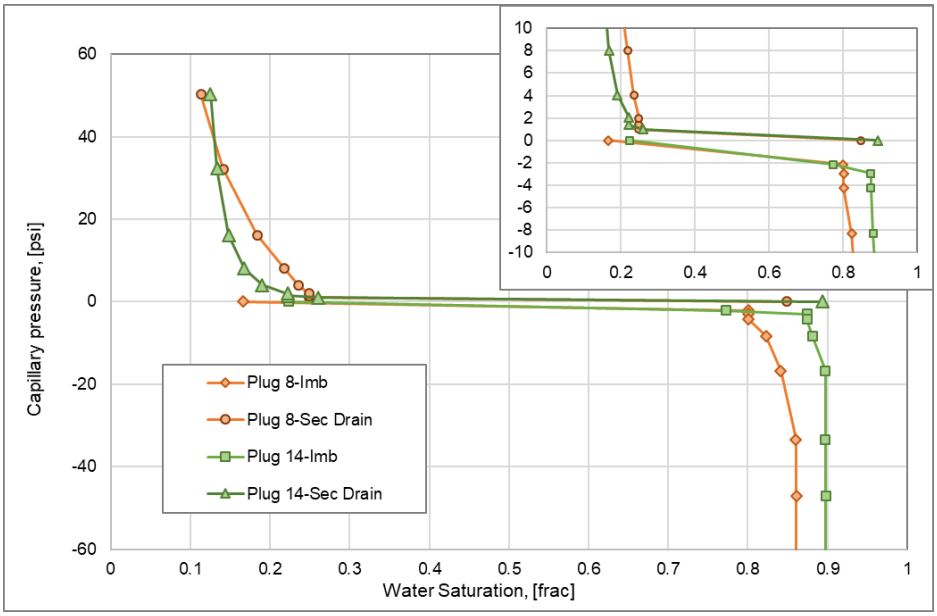

Figure 8: Oil-brine imbibition and secondary drainage capillary pressure measured by centrifuge on aged samples.

Table 7: Endpoint saturation and permeabilities after multi-speed centrifuge test

Routine Analysis			Primary Drainage		Imbibition		Secondary Drainage	
Sample Number	Porosity (%)	Klink Perm (mD)	S_{wi} (ave) (%Vp)	K_O @ S_{wi} (mD)	S_{or} (ave) (%Vp)	K_W @ S_{or} (mD)	S_{wi} (ave) (% Vp)	K_O @ S_{wi} (mD)
8 - PS 1	33.1	1264	0.166	717.3	0.152	586.4	0.163	841.1
14 - PS 2	33.4	2875	0.223	1505	0.106	2065	0.146	2179

5.2 Capillary pressure by Porous Plate:

The other two samples were utilized in Pc-RI experiments where capillary pressure was determined by the porous plate method. Samples saturated with Soltrol at S_{wi}, were mounted in core holders with a net overburden pressure of 115 bar. SFW at different pressure stages was injected from bottom. The top-end of the core is in capillary contact with an oil-wet membrane (porous plate) and it is only permeable to oil under pressure differentials less than the pore entry pressure of the membrane. Multi-step imbibition capillary at different saturations was measured, and then porous plate was removed and water permeability at residual oil saturation (K_W @ S_{or}) was measured. Afterwards, porous plate was replaced by a water-wet ceramic plate and Soltrol was injected to the core. Once equilibrium was achieved (this took few weeks), the pressure is increased, and the process repeated until a full curve of secondary drainage capillary pressure and resistivity index was obtained. Oil permeability at irreducible water saturation (K_O @ S_{wi}) was then measured and is given in Table 8.

Imbibition and secondary drainage capillary pressure curves is shown in Figure 9. Despite differences in petrophysical properties of sister plugs, for similar capillary pressure, generally lower residual oil saturation (after imbibition) and irreducible water saturation (after secondary drainage) was achieved by centrifuge experiment (see Table 7 and Table 8).

Table 8: Endpoint saturations and permeabilities after imbibition and secondary drainage porous plate test

Routine Analysis			Primary Drainage	Imbibition		Secondary Drainage	
Sample	Porosity	Klink Perm	S_{wi} (ave)	S_{or} (ave)	K_W @ S_{or}	S_{wi} (ave)	K_O @ S_{wi}
Number	(%)	(mD)	(%Vp)	(%Vp)	(mD)	(% Vp)	(mD)
7 - PS 1	34.1	2002	0.232	0.201	330.7	0.248	431.4
13 - PS 2	34.1	1045	0.242	0.209	350.1	0.180	1079

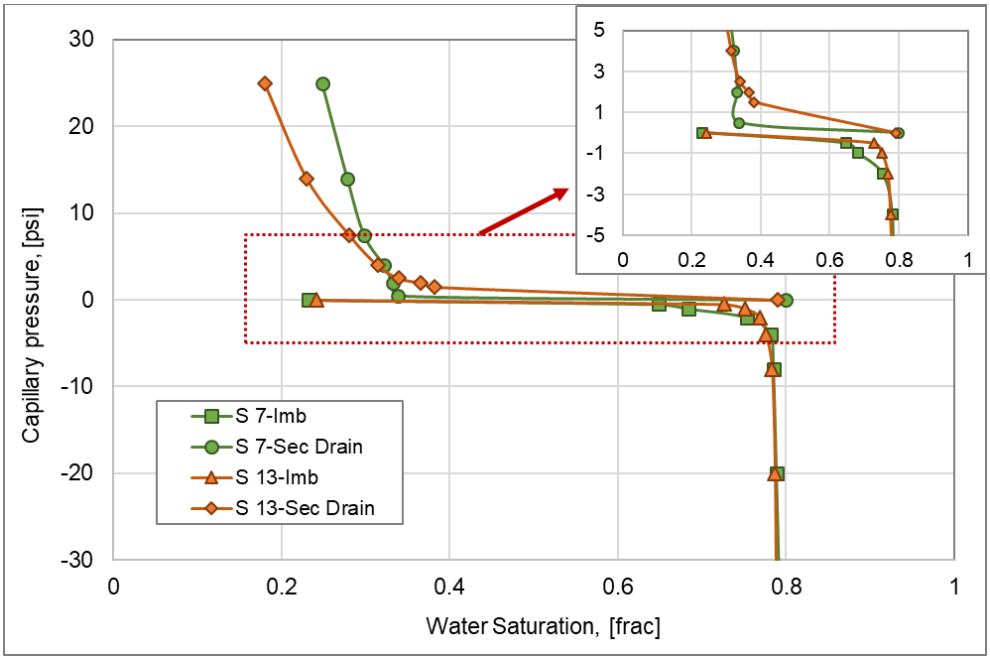

Figure 9: Oil-brine imbibition and secondary drainage capillary pressure measured by porous plate on aged samples.

6. Discussion

Four core samples (two sister plugs) were flushed-cleaned by two different cleaning methods; standard method (Program-1) and more aggressive method (Program-2). After cleaning, wettability was confirmed with combined Amott-USBM method as water-wet. The Amott-Harvey index showed similar wettability for the four samples, while the USBM index exhibit samples cleaned by Program-2 are more water wet compared to sample cleaned by Program-1.

For further investigation, 4 more core samples (two sister plugs) from similar preserved sample were flushed cleaned by Program-2. Then, the core samples were aged with crude oil at reservoir conditions to restore the in-situ wettability. Afterwards, to examine the core wettability state in terms of fluid flow, oil-brine imbibition and secondary drainage capillary pressure and end-point saturations and relative permeabilities were measured

with two different approaches; multi-speed centrifuge and porous plate.

Imbibition capillary pressure measured on aged and not aged samples from preserved sample 1 and 2 are compared in Figure 10 and Figure 11. Oil-brine imbibition capillary pressure was measured using centrifuge on plugs 2 and 4 from PS 1 and plugs 9 and 10 from PS 2, right after cleaning and without aging process. The plugs are strongly water-wet (as shown earlier in Table 3) and it explained the large increase in water saturation by spontaneous water imbibition. On the other hand, for plugs 7 and 8 from PS 1 and plugs 13 and 14 from PS 2 which are aged, almost no spontaneous water imbibition was observed. The wettability of these plugs is quantified as intermediate water-wet, although less than 1 psi capillary pressure was required to make a large shift in water saturation.

Considering the PS 1 is from oil zone and PS 2 is from water zone, hence the original wettability for these preserved samples was significantly different. Meanwhile, the cleaning and aging process has resulted in similar wettability behavior for both samples as it is shown in Figure 10 and Figure 11. Therefore, we believe the current rock wettability is entirely dependent on crude oil properties and interaction between rock and fluid. Since the aging time (4-weeks) is not comparable with geological time that porous media were exposed to oil, the current wettability might be underestimated toward oil-wet system.

End-point properties including residual oil saturation (S_{or}) and water permeability (K_{rw} @ S_{or}) at the end of water-flooding for aged and not-aged samples are compared Table 9 and Figure 12. For not-aged samples, K_{rw} @ S_{or} do not correlate with cleaning programs. Low K_{rw} @ S_{or} is simply due to strong water-wet system and it varies with core structures. For aged samples, residual oil saturation at the end of water flooding is lower and subsequently water relative permeability is higher reflecting big shift in end-points properties as wettability changes towards intermediate water-wet system.

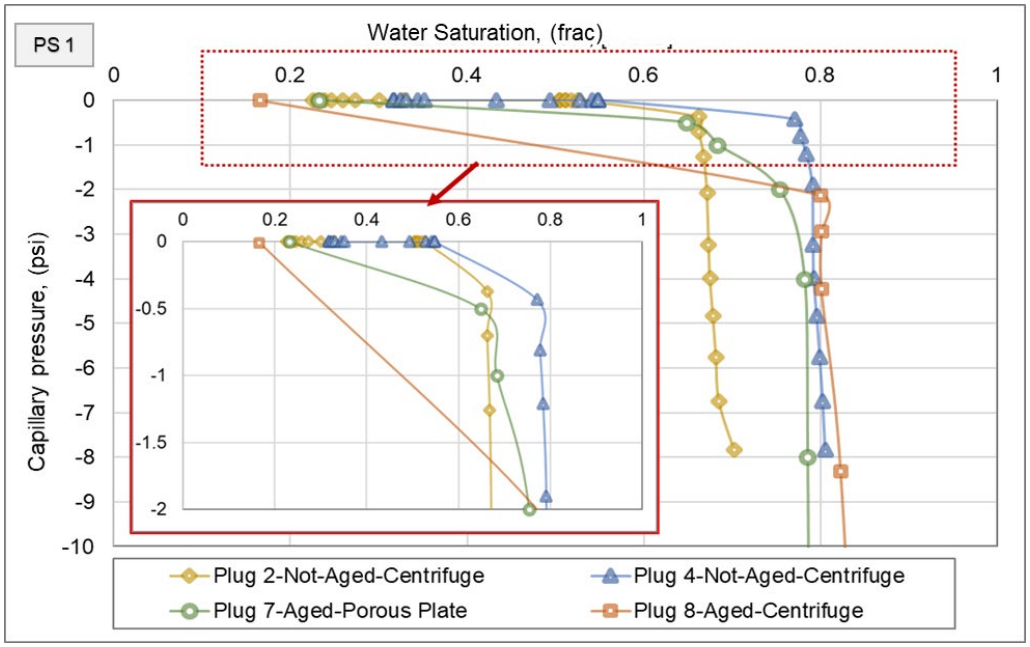

Figure 10: Oil-brine imbibition capillary pressure on sister-plugs from PS 1. Plug 2 (yellow line) is after cleaning program 1, plug 4 (blue triangle) is after cleaning program 2. Plug 7 (green circle) and plug 8 (orange square) are after cleaning program 2 and aging.

Table 9: initial and residual oil saturation and water relative permeability at end of water flooding

Sample No.	Aging [-]	Cleaning Program	He Poro. (% of Vb)	Klink Perm (mD)	S_{oi} (frac)	S_{or} (frac)	K_{rw} @ S_{or} (frac)
2-PS 1	×	Program 1	32.9	1644	0.800	0.298	0.07
4-PS 1	×	Program 2	32.3	1374	0.800	0.194	0.32
7-PS 1	✓	Program 2	34.1	2002	0.768	0.201	0.77
8-PS 1	✓	Program 2	33.1	1264	0.834	0.152	1.00
9-PS 2	×	Program 2	31.3	1373	0.750	0.296	0.08
10-PS 2	×	Program 1	31.0	1122	0.750	0.255	0.14
13-PS 2	✓	Program 2	34.1	1045	0.758	0.209	0.32
14-PS 2	✓	Program 2	33.4	2875	0.777	0.106	0.95

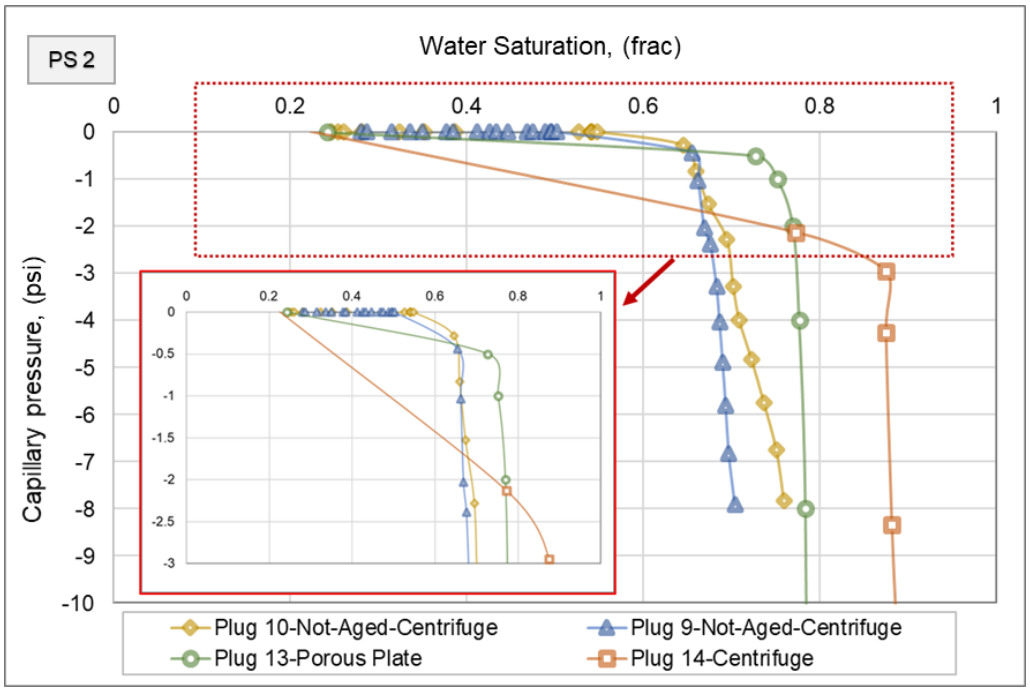

Figure 11: Oil-brine imbibition capillary pressure on sister-plugs from PS 2. Plug 10 (yellow line) is after cleaning program 1, plug 9 (blue triangle) is after cleaning program 2. Plug 13 (green circle) and plug 14 (orange square) are after cleaning program 2 and aging.

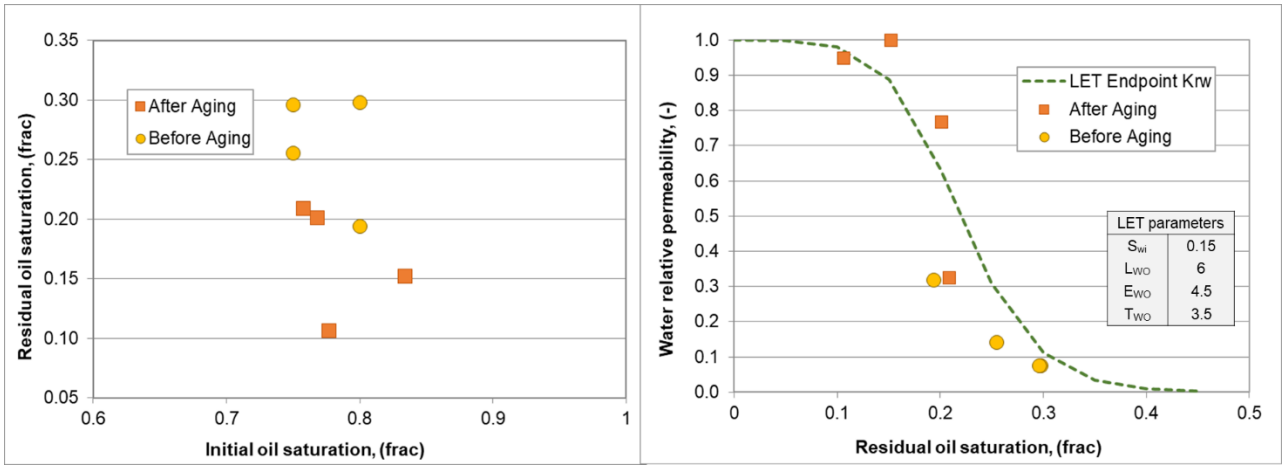

Figure 12: Residual oil saturation and water relative permeability at end of water flooding on aged and not aged samples.

7. Conclusion

In the presented work, effect of two cleaning approaches is studied in detail. Core plugs from two preserved samples with similar petrography and petrophysical properties, but one from oil zone and the other from water zone, were flush cleaned by two programs; Program-1 and Program-2. Gas chromatography analysis on effluents produced from the core plugs showed the presence of heavy hydrocarbon (fractions heavier than C_{42}) even after more than 40 PV solvent injection.

Wettability of the core plugs were then tested using combined Amott-USBM wettability method. The Amott-Harvey index does not show much different in wettability of the samples. But, the USBM index showed plugs cleaned by the Program-2 are more water-wet compared to those cleaned by Program-1. Spontaneous water imbibition and endpoint properties on clean samples before aging reflects the strong water-wet behavior but did not correlate with cleaning programs. Afterwards, two more plugs from each preserved sample were drilled and cleaned by program-2 and then aged at reservoir conditions. Oil-brine imbibition capillary pressure, endpoint saturation and relative permeability were measured by centrifuge and porous plate. Almost no spontaneous water imbibition was observed on these plugs and endpoint properties were greatly shifted towards intermediate water-wet system. Although the original wettability of the samples was not the same (one from oil zone and the other from water zone), the core treatment procedure resulted in almost similar water-oil flow properties.

Based on our observations, cleaning Program-2 removed more oil, especially heavy hydrocarbons, from the core than typical cleaning protocol so called Program-1. On the other hand, the elaborate Program-2 is often impractical, takes too long, is expensive and limited by laboratory capacity. We believe proper cleaning approach is specific to certain rock and fluid and should be derived separately for an oil field. An effective cleaning method can simply be confirmed by performing gas chromatography compositional analysis of the final effluent at the end of core cleaning.

Acknowledgements

This study is a part of ongoing SCAL (special core analysis) project on core plugs from an exploration well from Edvard Grieg oil field. Therefore, the authors would like to thank Lundin-Energy Norway and our partners, Wintershall Dea Norge and OMV Norge, for funding this project and for allowing to publish these data. We would also give special thanks to PanTerra Geoconsultants for performing the experiments and providing excellent advices.

References

[1] C. McPhee, J. Reed and I. Zubizarreta, *Core Analysis: a Best Practice Guide*, Amsterdam: Elsevier, 2015.

[2] E. Donaldson, R. Thomas and P. Lorenz, "Wettability Determination and Its Effect on Recovery Efficiency," **no. 13-20, 1969**.

[3] G. Hirasaki, J. Rohan, S. Dubey and H. Niko, "Wettability Evaluation During Restored-State Core Analysis," in SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 1990.

[4] E. Amott, "Observations Relating to the Wettability of Porous Rock," **Vols. 216, (156-162)**, 1956.

[5] W. Anderson, "Wettability literature survey - Part 2: Wettability measurement," **vol. 38:12**, 1986.

[6] W. Anderson, "Wettability Literature Survey - Part 4: Effects of Wettability on Capillary Pressure," **no. 1283-1300**, 1987.

[7] W. Anderson, "Wettability Literature Survey - Part 5: Effects of Wettability on Relative Permeability," **no. 1453-1468**, 1987.