

NEW METHOD TO CLEAN CARBONATE RESERVOIR CORES BY SEAWATER

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ABSTRACT

It was recently documented, that modelling of carbonate reservoirs for predicting waterflood performance, could be done by obtaining a reliable P_c curve based on primary drainage, which forms the basis for oil in place calculations and for modelling the imbibition P_c curve. Furthermore, a reliable primary drainage P_c curve was only obtained when the carbonate core was properly cleaned to improve the water-wet fraction significantly. Carboxylic material present in crude oil is bonded very strongly onto the carbonate surface. It is nearly impossible to use traditional solvents to clean the surface. A chemical reaction under irreversible thermodynamic conditions is needed to remove the material. A series of preferential oil-wet limestone cores from a Middle Eastern oil reservoir was first cleaned by the traditional technique using toluene and methanol. Thereafter, the cores were flooded with different PVs of synthetic seawater, SW, at 130 °C. The newly developed chromatographic wettability test showed that the water-wet fraction can increase by about 30% after flooding with SSW at high temperature. Seawater is, however, known to act as a wettability modifier in chalk, which will improve oil recovery by spontaneous imbibition. It is therefore interesting to note that SW also can act as a cleaning solvent. It is also confirmed that a rather small increase in the water-wet area may have a significant effect on oil recovery by spontaneous imbibition.

INTRODUCTION

Seawater is known to act as an EOR-fluid towards chalk in the sense that it is able to improve water wetness, which will increase oil recovery during a water flood (Zhang and Austad 2006; Zhang et al. 2006). The chemical mechanism has been described as an interaction between active ions in seawater (Ca^{2+} , Mg^{2+} , SO_4^{2-}) and the rock surface. Some of the strongly adsorbed carboxylic material is then removed from the chalk surface (Zhang et al. 2007). The efficiency of the wettability alteration process is sensitive to the temperature, and a temperature above 90-100 °C appeared to be needed. Cleaning of carbonate cores has always been an issue for debate, because of the very strong interaction between the carboxylic components and the calcite surface. It was recently documented, that modelling of carbonate reservoirs for predicting waterflood performance could be done by obtaining a reliable P_c curve based on primary drainage, which forms the basis for oil in place calculations and modelling of the imbibition P_c curve (Masalmeh and Jing 2007). Furthermore, a reliable primary drainage P_c curve was only obtained when the carbonate core was properly cleaned to improve the water-wet fraction significantly.

The question that we ask in this paper is: “Can seawater be used to improve the cleaning of carbonate cores, i.e. to improve the water wetness after performing the traditional cleaning procedure using MeOH and toluene ?”

EXPERIMENTAL

Carbonate rocks

In the experiments outcrop chalk and reservoir limestone cores have been used.

Chalk cores: All chalk cores were prepared from the same Stevns Klint chalk block and used in the experiments. The chalk consists of 98 % pure biogenic CaCO₃ with high porosity (45-50 %) and low matrix permeability (2-3 mD). It has a reactive large surface area of about 2 m²/g (Frykman 2001; Røgen and Fabricius 2002). The age and properties of the chalk are quite similar to those observed for the North Sea chalk oil reservoirs. The data for the cores are given in Table 1.

Limestone cores: The physical properties of the reservoir limestone cores from a field in the Middle East are summarized in Table 2. Prior to use, the cores were cleaned at ambient temperature by flooding with water-saturated toluene (at least 5 PV) at a rate of 0.1 ml/min until the effluent was colorless (min. 3 PV). Thereafter, the cores were flooded with 3 PV of methanol also at ambient temperature, and finally dried at 110 °C to constant weight.

Brines

Artificial formation water, VB, related to the Valhall field was used as initial brine in the imbibition and wettability experiments on the chalk cores. The compositions of synthetic seawater, SW, and the chromatographic fluids SW-U, SW¹/₂M and SW-M are given in Table 3.

Oils

Two different oils have been used in the experiments. Heptane was used as a reference oil to represent a water-wet core. A reservoir stock tank oil diluted with 40 vol% n-heptane, centrifuged, and filtered through a 5 µm Millipore filter, was used in the chalk experiments with neutral-wet chalk cores. This mixture has been used in many previous experiments, and no precipitation of asphaltenic material was detected on standing. Heptane was used to keep the viscosity of the oil closer to reservoir conditions. The oil was termed RES40~1.6, and the acid number, AN, was 1.6 mg KOH/g, the density was 0.805 g/cm³, and the viscosity was 2.5 cP. The high AN of the oil made the carbonate rock neutral to oil-wet.

Preparation of the chalk cores

The chalk cores were prepared according to the method described in a previous paper (Punternold et al. 2007). The cores were flooded with distilled water to remove any dissolvable salts, especially sulfates, and then saturated with formation water VB. Initial water saturation was established by flooding the cores in a Hassler core holder with 1.5 PV of oil in each direction. The crude oil saturated cores were wrapped in Teflon tape and

aged in the oil at 90 °C for 4 weeks in a sealed steel container. The core data are listed in Table 1.

Spontaneous imbibition

The oil saturated cores were transferred to a sealed steel imbibition cell and surrounded with the imbibing fluid. The spontaneous imbibition test (SI) was performed at the specified temperature with a constant back pressure of ~10 bar. The produced oil was collected in a burette, and the volume was recorded as a function of time.

Chromatographic wettability test

The chromatographic wettability test, developed by (Strand et al. 2006), which determines the water-wet surface area of a chalk core, was used to determine changes in the wetting condition. The same test is also valid for limestone cores (Punternvold 2008; Strand et al. 2008). The oil saturated carbonate core was placed inside a Hassler core holder and flooded with SW brine without sulfate (SW-U) to obtain residual oil saturation, S_{orw} . Next, the core was flooded with SW brine containing both SO_4^{2-} and SCN^- as a tracer (SW-M or SW $\frac{1}{2}$ M) at a constant rate. The effluent was collected using a fraction collector. Each fraction was analyzed for SO_4^{2-} and SCN^- , and the concentration relative to the initial concentration was plotted against injected pore volumes, PV. Chromatographic separation between the non-adsorbing tracer SCN^- and the adsorbing SO_4^{2-} takes place at the water-wet sites of the chalk surface, and the area between the elution curves of the two components is directly proportional to the water-wet area inside the core. Completely water-wet condition is assumed when using heptane as the oil phase in outcrop cores not exposed to oil.

Chemical analysis

The ionic concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} , and SCN^- in the effluent fraction from the chromatographic wettability test were analysed using an ion-exchange chromatograph, ICS-3000 Reagent-free™ produced by Dionex Corporation, USA. The effluent samples were diluted 1:10 or 1:20 by deionised water prior to the analyses, and the ionic concentration was calculated by the use of external standards.

RESULTS AND DISCUSSIONS.

This section is organized by first presenting the results from core studies using outcrop chalk to document the potential of seawater to change wetting condition. Then, the potential of seawater as a core cleaning fluid will be presented using reservoir limestone cores.

Seawater as wettability modifier in chalk

Three similar outcrop cores from the same block were used. One of the cores was used as a reference core for a water-wet system by using heptane as the oil phase. The chromatographic wettability test was used, and the validation of this test for carbonates has been reported previously (Strand et al. 2006) The area for the chromatographic separation

between the tracer and sulfate when flooding seawater with tracer, SCN^- , was calculated to be $A=0.170$, Fig. 1.

The two other cores were saturated under vacuum with Valhall reservoir brine (VB) without any SO_4^{2-} . The initial water saturation was decreased to $S_{wi} \sim 0.25$ by flooding, 1.5 PV in each direction, using a crude oil with a high acid number ($\text{AN} = 1.60 \text{ mgKOH/g}$). Finally, the cores were aged in the crude oil at 90°C for 4 weeks.

After aging, one of the cores (VF#35) was flooded to residual oil saturation, $S_{or} = 0.25$, at room temperature using seawater without any sulfate (SW-U) and the wettability was determined chromatographically. The area between the tracer and the sulfate curve was determined to be, $A=0.103$, Fig. 1, which corresponds to a water-wet fraction of $\text{WI} = (0.103/0.170) = 0.61$.

After aging, the third core (VF#32) was imbibed by Valhall brine at 90°C , and the oil recovery was very low, less than 10% of OOIP, Fig. 2. No improvement in oil recovery was detected when the imbibing fluid was switched to seawater (SW) at 90°C . When the temperature was increased to 130°C , seawater imbibed spontaneously, and the plateau recovery was slightly below 50 % of OOIP. Obviously, the temperature of 90°C is too low for wettability alteration in an imbibition process.

The core was removed from the imbibition cell and flooded to S_{or} with SW-U. The flooding continued until no sulfate was detected at the outlet using a BaCl_2 solution. Finally, the new wetting condition was determined chromatographically, and the area between the tracer curve and sulfate curve was calculated to be, $A=0.188$, Fig. 1, which corresponds to a water wet fraction of $\text{WI} = (0.188/0.170) = 1.1$. Thus, by exposing the core to SW at 130°C for about 20 days, the wetting condition has been changed drastically. The wetting properties appeared to be quite similar to the reference water-wet core saturated with heptane, which was supposed to be completely water-wet.

Wettability modification by seawater in limestone

All the reservoir limestone cores used in these tests were pre-flooded with toluene and MeOH. Thus, the objective of the experiments is to document that seawater at high temperature is able to improve the water wetness after cleaning the cores in the traditional way. Three sets of experiments were conducted.

The wetting state of the 46A core was determined by the chromatographic technique before and after the core was used for various tests at both low and high temperatures with SW (Punternvold 2008; Strand et al. 2008). The wettability tests were performed at room temperature using the brine termed SW $\frac{1}{2}$ M. The chromatographic separation between SCN^- and SO_4^{2-} before the core was exposed to SW at high temperatures is shown in Fig. 3. The area between the tracer curve and the elution curve for SO_4^{2-} , which is proportional to the water-wet area, was estimated to be $A=0.107$. The fact that the tracer curve passes through the coordinate (1.0, 0.5) indicates that the total pore volume of the core was connected and flooded by the injected fluid. The wettability test of the same core after the core had been exposed to SW at both low and high temperatures (the core was flooded with at least 6 PVs of SW at 130°C), is shown in Fig. 4. The water-wet surface area has

increased because the calculated area between the tracer and sulfate curve was increased to $A=0.141$, which corresponded to an increase in the water wetness of 32 %.

The limestone core termed C#20A appeared to be nearly completely oil-wet after cleaning with toluene and MeOH since the separation between the elution curve for the tracer and sulfate is negligible, as illustrated in Fig. 5. The core was flooded with seawater at 130 °C for 1 day, which corresponds to 3 PVs. After removing the sulfate by flooding with seawater without sulfate at ambient temperature, the chromatographic wettability test showed good separation between the tracer and the sulfate curve, Fig. 5. Thus, the water-wet area was increased significantly. After flooding the core a second time with seawater at high temperature for 3 days (9 PV), the chromatographic test did not show any significant increase in the water-wet area, as illustrated by the fact that the two elution curves for sulfate were similar, Fig. 5. It is, however, not correct to conclude that the core has obtained a completely water-wet condition, but there is no doubt that seawater at high temperature is able to remove strongly adsorbed carboxylic materials from the carbonate surface.

In the third set of wettability tests with limestone, the core termed C#33A showed a very large separation between the tracer and sulfate in the wettability test, Fig. 6, which indicated that this core appeared to be rather water-wet. The area between the two curves was $A=0.14$. After flooding the core with distilled water to remove salt, the core was dried at 110 °C, and saturated with decane. The core was then imbibed with SW-U at 70 °C, and the oil recovery reached a plateau of about 3.3% of oil in place, Fig. 7.

The core was then dried and washed with SW-U prior to a new injection of SW at high temperature. The core was flooded 9 PV (3 days) with seawater at 130 °C. A new wettability test only showed a slight increase in the area between the tracer and sulfate curve, $A=0.16$, which corresponded to an increase in water wet area of about 14%, Fig. 6. Finally, the core was subjected to a new imbibition test using decane and the same core preparation as in the first imbibition test. As seen in Fig. 7, the oil recovery increased compared to the first test prior to the high temperature flooding with seawater, from 3.3 % to about 8 %. Thus a rather small increase in the water-wet area may have an effect on oil recovery in a spontaneous imbibition process.

It appears to be a discrepancy between the low oil recovery by spontaneous imbibition and wettability. We have, however, previously observed that chalk samples containing significant amount of silica appeared to be very water-wet by using the chromatographic test, but the imbibition of water was very low (Strand et al. 2006). May be this core contained some silica, but this is only speculations.

General comments

Previous studies have shown that seawater acts an EOR fluid in chalk (Zhang 2006; Puntervold 2008). Preliminary chemical tests have also indicated that seawater may act as an EOR fluid in limestone. The same chemical interaction between seawater and the rock is observed in both cases, but the reactivity towards limestone is somewhat slower than for

chalk (Strand et al. 2008). The results from the present paper support these observations, and seawater can even be used to improve the cleaning of reservoir limestone cores.

Carboxylates from the crude are strongly adsorbed onto the carbonate surface, and traditional cleaning of reservoir carbonate cores by using toluene and methanol will not remove all the adsorbed material. Obviously, each of the limestone cores showed different wetting properties after being cleaned with toluene and MeOH. The reason may be that we have used some of the cores in previous experiments in combination with the cationic surfactant, C12TAB, as wettability modifier. It is previously documented that this surfactant is able to improve the water wetness in chalk and dolomite (Standnes and Austad 2000; Standnes et al. 2002).

During the restoration of the wetting condition of a pre-cleaned carbonate core, it is very important to be aware of the strong impact of sulfate on the final wetting properties. If the initial water saturation is established by drainage using water saturated N₂ gas and porous plate, the concentration of sulfate in the residual water will increase due to the adsorption of sulfate onto the carbonate surface. Sulfate in combination with divalent ions like Ca²⁺ and Mg²⁺ increases the water wetness of the core (Punternvold et al. 2007). This is clearly demonstrated in Fig. 8. One of the chalk cores was pre-flooded with distilled water to remove traces of sulfate initially present, and the core appeared less water wet compared to the core not pre-flooded with distilled water.

CONCLUSIONS

The strong chemical interaction between seawater and calcite surface is further documented in this paper, and the following conclusions can be made:

- Chalk of neutral wetting condition will act as completely water-wet after exposing to seawater at 130 °C in a spontaneous imbibition process.
- The water-wetness of reservoir limestone cores pre-cleaned at ambient temperature with toluene and MeOH can be drastically improved by flooding with seawater at 130 °C.
- The observed wetting modification with seawater in limestone supports previous observations that seawater can act as an EOR-fluid also in limestone

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Table 1. Core data for chalk cores.

Core ID	L [cm]	D [cm]	V_b [cm ³]	Φ [%]	k [mD]	PV [ml]	S_{wi} [%]	Oil [ml]	S_{or} [%]
VF#20	6.72	3.81	76.6	48.8	~2	37.49	35	Heptane	30
VF#32	6.77	3.79	76.3	47.5	~2	36.3	22	Crude	29
VF#35	6.79	3.79	76.6	48.5	~2	37.1	27	Crude	24

Table 2. Core data for reservoir limestone cores.

Core ID	L [cm]	D [cm]	V_b [cm ³]	Φ [%]	k [mD]	PV [ml]
20A	4.88	3.78	54.76	25.95	8.47	14.21
33A	4.67	3.78	52.41	28.57	6.22	14.97
46A	4.76	3.78	53.42	27.8	2.47	14.8

Table 3. Composition and properties of the brines used.

Ions	VB mole/l	SW mole/l	SW-U mole/l	SW ^{1/2} M mole/l	SW-M mole/l
HCO_3^-	0.009	0.002	0.002	0.002	0.002
Cl^-	1.066	0.525	0.623	0.574	0.525
SO_4^{2-}	0.000	0.024	0.000	0.012	0.024
SCN^-		0.000	0.000	0.012	0.024
Mg^{2+}	0.008	0.045	0.045	0.045	0.045
Ca^{2+}	0.029	0.013	0.013	0.013	0.013
Na^+	0.997	0.450	0.500	0.475	0.450
K^+	0.005	0.010	0.010	0.022	0.034
IS	1.11	0.66	0.68	0.68	0.68
TDS, g/l	62.83	33.39	35.72	35.72	35.7

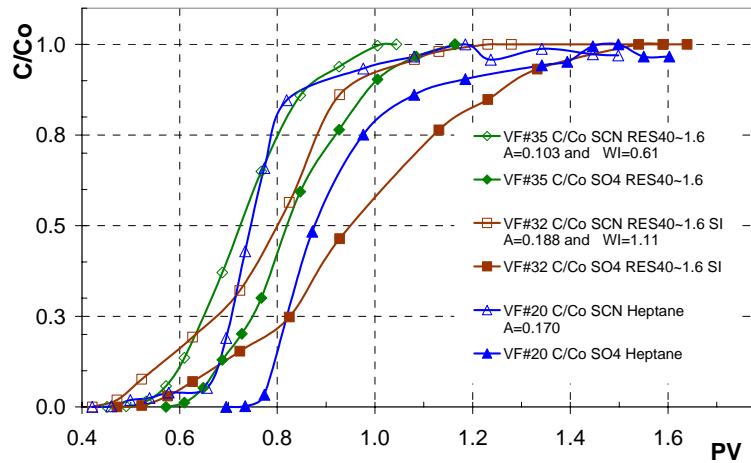


Figure 1. Comparable wettability indices for cleaned chalk cores, before (VF#35) and after (VF#32) SI at 130 °C. $S_{wi} \sim 0.25$. Crude oil with AN = 1.6 mg KOH/g. The heptane saturated core, VF#20, is used as a reference for a water wet core ($A = 0.17$). The cores were flooded with SW-M at a rate of 0.2 ml/min

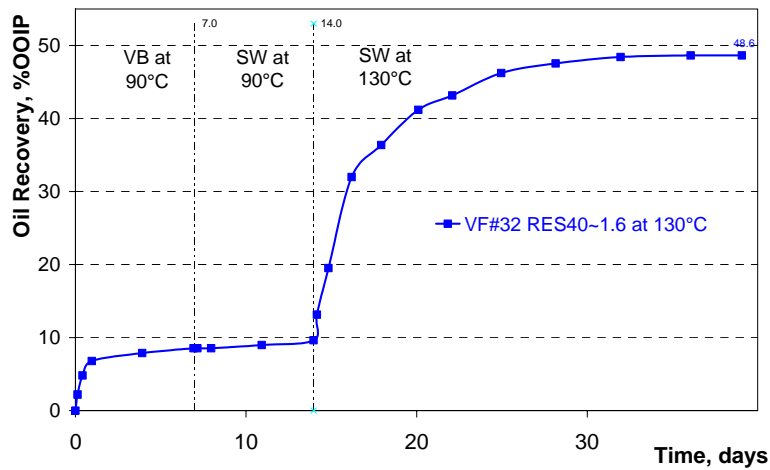


Figure 2. Stevns Klint core VF#32 ($S_{wi} \sim 0.25$) saturated with RES40 oil with AN~1.6 and aged for 4 weeks at 90 °C. The core have been SI at 130°C giving an oil recovery of 49%

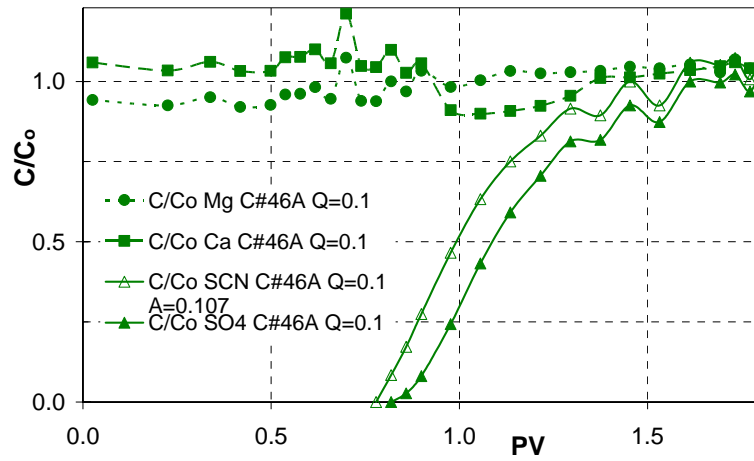


Figure 3. Chromatographic wettability test on core 46A before exposure to SW at high temperature. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. (Strand et al. 2008)

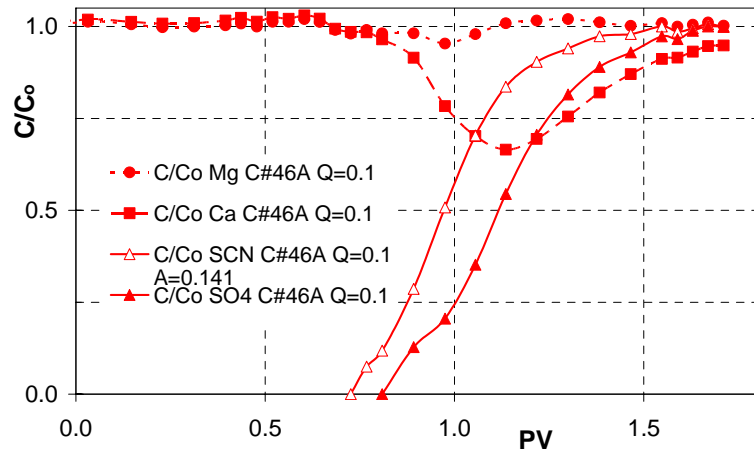


Figure 4. Chromatographic wettability test on core 46A after exposure to SW at high temperature. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. (Strand et al. 2008)

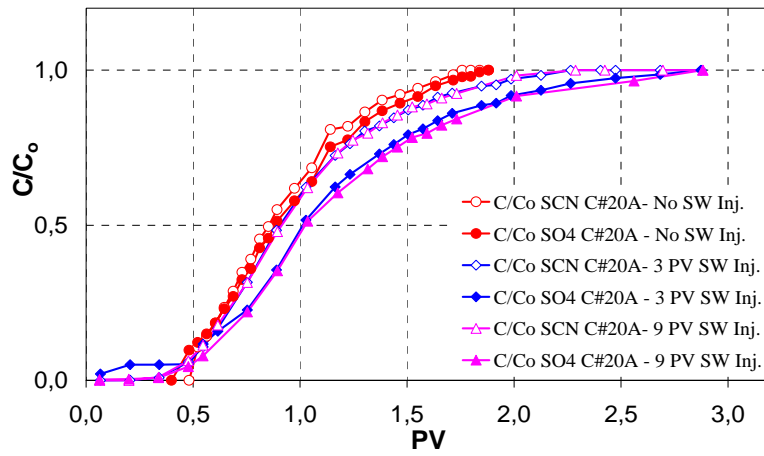


Figure 5. Three Chromatographic wettability tests on core C#20A. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. The results shows the water wet area before exposure to SW at high temperature, and after 3 PV (1 day) and after 9 PV (2 days) injection of SW.

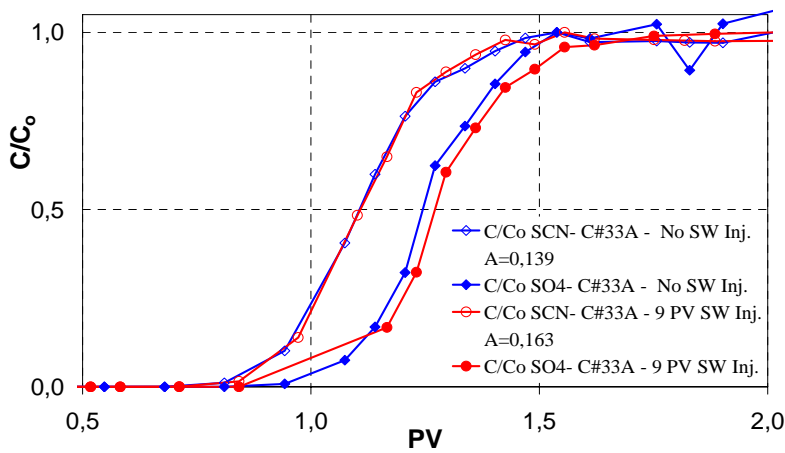


Figure 6. Chromatographic wettability tests on core C#33A. The core was flooded with SW $\frac{1}{2}$ M at a rate of 0.1 ml/min. The results shows the water wet area before exposure to SW at high temperature and after 9 PV (3 days) injection of SW.

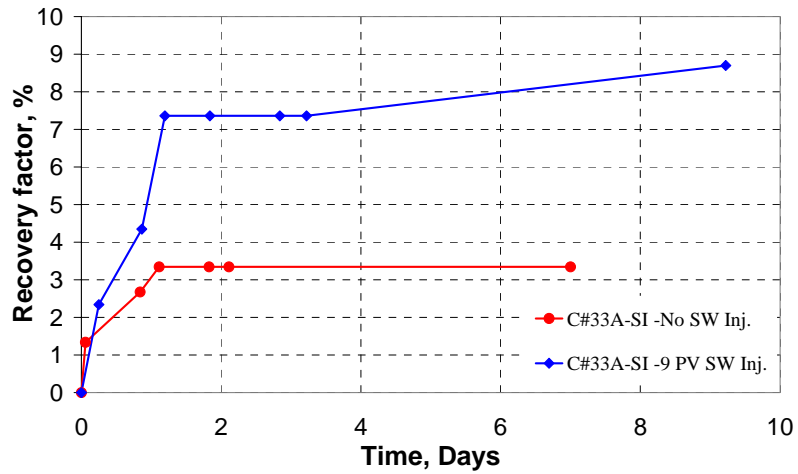


Figure 7. Spontaneous imbibition at 70 °C of decane saturated core C#33A before exposure to SW at high temperature and after 9 PV (3 days) injection of SW.

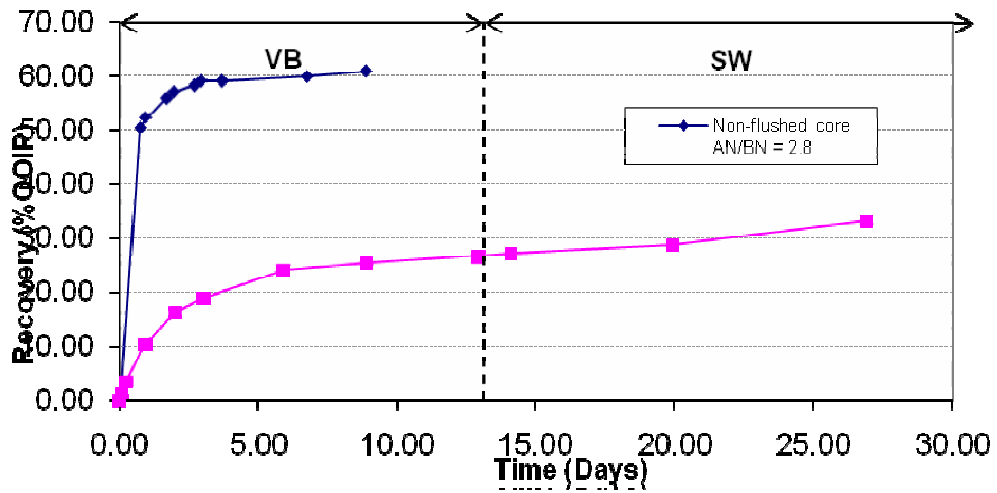


Figure 8. Imbibition at 90 °C into non-cleaned and cleaned cores. The cores were first imbibed with formation brines (VB), followed by SW. The cleaned core appeared to be much less water-wet than the non-cleaned core. $S_{wi} \sim 0.1$. Crude oil with AN = 0.5 mg KOH/g (Puntervold et al. 2007).