

REMOVAL OF MUD COMPONENTS FROM RESERVOIR SANDSTONE ROCKS

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ABSTRACT

Laboratory experiments using reservoir rock/oil are used extensively to estimate reservoir oil recovery processes. Mud contamination of the reservoir rock can change the flow conditions by changing the rock surface chemistry and permeability. Representative data can then only be generated if mud contamination is removed. The objective for study was to investigate the removal of these mud components during cleaning of sandstone reservoir core plugs. Effluent samples were analysed, and wettability of cleaned core plugs was characterized. Samples of core plugs after cleaning and after water flooding were analysed by scanning electron microscopy (SEM) and the oil residue in cleaned reservoir rock was analysed by gas chromatography.

When formation water (FW) was injected to uncleaned or solvent cleaned reservoir core plugs with potential contamination by water-based mud, ions from the mud were produced for relatively long periods. SEM analyses showed that polymers, clay and barite from the mud were present in the pores of cleaned high permeability reservoir core plugs. Even after water flooding, mud components were found in this rock. Polymers and particles can reduce the permeability of the rock. Invasion of clay from the mud will increase the surface area and ion-exchange capacity of the rock. Clay invasion and/or wrong FW composition can affect the established wettability and thereby the estimated potential for water flooding and EOR methods.

Contamination of sandstone rocks with oil-based mud was shown to alter the wettability. Emulsifiers from the mud were slowly removed during cleaning by crude oil injection. The cleaning procedure for reservoir rock with potential oil-based mud contamination, was shown to affect the measured capillary desaturation curve.

Mud components should be removed during cleaning of the reservoir core plugs, otherwise the core plugs should not be used. Analyses of effluent samples for these components during core plug preparation should be included in the standard preparation procedures. For some mud components, chemical analysis can be challenging. The cleaning procedure should also be evaluated for the actual reservoir rock by analysing cleaned core plugs for wettability, oil residue and mud components. Important minerals should not be removed from the original reservoir rock during cleaning.

INTRODUCTION

Both pressure and temperature are reduced during retrieval of reservoir rock samples [1]. This can change the solubility of minerals and organic and inorganic components in the residual reservoir fluids. A gas phase will also be formed when the pressure is reduced below bubble point. Invasion of mud components can alter the rock properties [2]. Wettability can be changed by adsorption of mud components. Invasion of particles, polymer and resins from the mud can also reduce the permeability of the rock. The ionic composition of the brine in the mud system is different from the formation water (FW) composition. The surface properties of the minerals can therefore be changed due to mud filtrate invasion. In the preparation of reservoir rock in the laboratory it is important to establish wettability conditions representative of the oil reservoir [2]. Mud contamination and precipitates from the reservoir fluids should be removed, prior to testing. It is important that the selected composition of the FW is as similar as possible to the real reservoir FW. Preparation of the reservoir rock with incorrect compositions of the FW can give unrepresentative surface properties of the minerals and thereby wettability conditions which are not representative of the reservoir.

The first aim of the presented study was to evaluate the cleaning procedure of high permeability reservoir sandstone core plugs with potential contamination by water-based mud. The second aim was to explore cleaning of sandstone rock (medium permeability) with oil-based mud contamination. Another reservoir sandstone rock with the potential contamination with oil-based mud was cleaned by different procedures before determination of the capillary desaturation curve.

METHODS

Water-Based Mud: Evaluation Cleaning Procedure

The procedure for cleaning of high permeability reservoir sandstone rock with potential contamination by water-based KCl mud was evaluated using core plugs drilled from the same seal peel parallel to bedding.

Cleaning

The core plugs were first flooded with synthetic formation water (SFW, Table 1) in tri-axial core-holders at 60°C using injection rate of 0.5ml/min. The core plugs were then cleaned by methanol/toluene cycles at 60°C with an injection rate of 0.5ml/min until the effluent was colourless, 4 cycles with 5 pore volumes (PV) of each solvent in each cycles. The total period with cleaning was approximately 6 weeks, including injection and storage. The cleaning was finished with a 17 PV injection of methanol. The methanol was then replaced with SFW at room temperature at an injection rate of 0.5 ml/min, before absolute permeability was determined. Effluent brine samples were analysed for elements by Inductively Coupled Plasma (ICP) in both SFW injection steps.

Analyses Of Cleaned Reservoir Cores

Spontaneous imbibition and forced imbibition experiments were performed to characterize the wettability of cleaned core plugs. After drainage to S_{wi} by Isopar H

(synthetic oil) using the confined porous plate method the spontaneous imbibition of SFW was studied in Amott cells at room temperature. Water flooding with SFW was then carried out in tri-axial core-holder at room temperature. Samples from inlet, mid and outlet of one cleaned core plug were extracted with dichloromethane, and the extracts were analysed by gas chromatography to characterize the oil residue. Distribution of mud components from inlet to outlet of cleaned reservoir core plug was studied by a ZEISS Supra 35 VP field emission SEM. An EDAX Energy-dispersive X-ray spectroscopy (EDS)-detector was used for analyses of the elemental composition.

Oil-Based Mud: Evaluation Cleaning Procedures

Cleaning By Stock Tank Oil Injection

Sandstone core plugs (100-200mD) drained to S_{wi} were aged with STO at 90°C for 14 days. Oil-based mud filtrates were prepared by stepwise filtration from 120 μ m down to 5 μ m. The mud filtrate was injected to core plugs through an inlet filter of 0.45 μ m using an injection rate of 0.5ml/min. The rock was then aged again for 14 days at 90°C before cleaning by STO injection. Emulsifier production was studied by determination of the interfacial tension (IFT) between the effluent oil phase and SFW using the spinning drop technique [3]. Wettability after this cleaning was then characterized by spontaneous imbibition of SFW.

Capillary Desaturation Curve With Different Solvent Cleaning

To evaluate the potential for surfactant flooding in a sandstone reservoir, capillary desaturation curve (CDC) was determined. Two different cleaning procedures were used for the reservoir rock with potential contamination by oil-based mud: 1. Injection of methanol until colourless effluent, and 2. Injection of methanol/toluene (33pore volume (PV)), acetic acid (33PV) and ethanol (33PV). After cleaning, the composite reservoir core was saturated with isopropanol. Fluid systems of different IFT were prepared using solvent systems of 2w%CaCl₂/iso-octane/isopropanol [4, 5]. It was assumed that the solvent system has similar flooding behaviour at reduced IFT as surfactant systems.

RESULTS

Water-Based Mud: Evaluation Cleaning Procedure

Analysis of effluent samples and cleaned reservoir rock were carried out in the evaluation of the cleaning procedure for high permeable reservoir rock with potential contamination with water-based mud.

Element Composition Of Effluent During SFW Injections

SFW was first injected before cleaning with solvents to remove water-soluble mud components. In the beginning the effluent potassium (K) concentration was much higher than in injected SFW (Figure 1a) The K concentration gradually reduced, but was still higher than in SFW at the end of this injection step. In the beginning of the second SFW injection after solvent cleaning, the K concentration was also higher than injected before it became similar in the levels in SFW. These results show that the core plugs were contaminated by KCl-mud, and that all the contamination was not removed during the

solvent cleaning. Before solvent cleaning the effluent sulphur (S) concentration was also much higher than in SFW at the start of injection, and was still higher than in SFW at the end of this step (Figure 1b). When SFW was injected the second time, the S-concentration was still higher than in SFW at the start of injection but became similar at the end of the injection. The development in effluent concentrations of K and S were rather similar in the first SFW injection (Figure 1), and the sulphur source is therefore probably the mud.

During the first SFW injection the effluent calcium (Ca) concentration was lower than in SFW, but at the end of this injection step was similar to the concentration in SFW (Figure 1c). This also confirmed the mud invasion, because the concentration of Ca in the mud filtrate is lower than in SFW. In the second SFW injection after solvent cleaning, the Ca concentration was largely stable. In the first SFW injection the effluent magnesium (Mg) concentration was also lower than injected and was still approaching the SFW level at the end of this step (Figure 1d). This again confirmed the mud contamination. At the end of the second SFW injection, the Mg concentration was similar as in SFW. The mud contamination was also confirmed by low effluent sodium (Na) concentration in the beginning of the first SFW injection and was still approaching SFW level at the end of this step (Figure 1e). At the end of the second SFW injection, the effluent Na concentration was as in SFW.

It is the water soluble mud components that should be easiest to remove during injection of SFW, especially the ions. The ICP-analysis of effluent samples during the two steps with SFW injection, clearly show that it is necessary to inject several pore volumes to remove the mud contaminations. It would have been more difficult to remove these mud contaminations from more heterogeneous core plugs. The results in the first SFW injection also indicated that cleaning of core plugs with only injection of SFW and crude oil, will require many pore volumes of SFW to remove the mud contaminations.

SEM-Analysis

After cleaning with solvents, inlet, mid and outlet samples of reservoir core were analysed by SEM. Examples of SEM-images are shown in Figure 2. Clusters of barite, clay and polymers were found in some samples. Bentonite clay in the mud has similar elemental composition as other clay minerals, and is difficult to identify by the used SEM-method. Since clay was found together with barite particles, it is likely that the samples also contained bentonite. In the images, polymers similar as in the reference samples were found. The SEM-images showed that the reservoir core plugs contained mud components even after cleaning with solvents. The elemental compositions based on EDS-spectra of the cleaned reservoir rock samples are given in Table 2. Since all samples contained barite, Ba and S were present in the samples. No systematic variation of elemental concentrations from the inlet to outlet was found. The reservoir core plugs were also drilled from the seal peel in the longitudinal direction. In another study reservoir cores were also cleaned by toluene/methanol cycles before they were drained to S_{wi} , aged with STO and used in water flooding experiments. After new toluene/methanol

cleaning after water flooding, the core plugs were also found to contain mud contaminations. See examples of SEM-images in Figure 3.

Oil Extract

Chromatogram of crude oil showed typical crude oil pattern of n-alkanes at least up to C₄₁ (Figure 4a). The GC-analysis of extracts showed that crude oil components were still present in the core plug even after cleaning with toluene/methanol cycles (Figure 4b, c and d). Since mainly high molecular weight components were present in the cleaned reservoir rock, it indicated precipitates of these components which were difficult to remove during cleaning with toluene/methanol cycles. Since the amount of extractable material was increasing from inlet to outlet in the core plug (Table 3), it appears that the solubility with these oil components has been low.

Spontaneous Imbibition And Forced Imbibition

To confirm that toluene/methanol cleaning resulted in water-wet rock, spontaneous and forced imbibition were studied by preparing two cleaned reservoir core plugs using Isopar H (synthetic oil) as oil. Established S_{wi} was similar for the two core plugs, 0.18 and 0.19 respectively. The spontaneous imbibition was rather high and fast for both core plugs (Figure 5). When viscous flooding was carried out with SFW after the spontaneous imbibition experiments, no additional oil was produced. Increase in the injection rate from 3 to 7ml/min gave no oil production and the differential pressure across the core plugs was rather stable at the different rates. No capillary end effects were therefore observed. These results showed that the core plugs were water-wet.

Even though the cleaned core plugs were found to be water-wet, the wettability after aging with crude oil may be affected by invasion of mud particles. Barite has rather small area/weight ratio, and will be water-wet. Clay has high area/weight ratio and invasion of bentonite clay will increase the surface area. Aging with crude oil may therefore give less water-wet conditions than without invasion. In addition, invasion of mud particles may have altered the permeability.

Oil-Based Mud: Evaluation Cleaning Procedures

Cleaning With STO Injection

Sandstone core plugs were first aged with STO at S_{wi} . When STO was displaced by the mud filtrates, the oil permeability was only slightly changed (Table 4). After new aging for 14 days, the mud filtrate was replaced by STO. The oil permeability then became only slightly higher than before the exposure to the mud filtrates. Minor changes in oil permeability was observed when STO was injected instead of mud filtrate in the reference core plug. For the core plug exposed to the mud filtrate with mineral base oil (MFM), the STO injection was stopped after approx. 4PV, because the differential pressure across the core plug was stable. IFT between the oil-phase effluent and SFW was at this point in the same range as between MFM and SFW (Figure 6a). This means that at least one emulsifier was still released from the rock, and equilibrium conditions were not established inside the core plug. For the core plug exposed to the mud filtrate

with synthetic base oil (MFS), IFT was found to increase from approx. 3PV to approx. 7.3PV (Figure 6a). IFT was then still lower than between STO and SFW. This also showed that at least one emulsifier was produced during a rather long period with back-production. The release of emulsifier(s) was therefore slow in both plugs exposed to mud filtrate. After cleaning with STO injection, the wettability of the core plugs was characterized by spontaneous imbibition of SFW. The spontaneous imbibition of SFW was in the beginning slower for the core plugs exposed to mud filtrates than for the reference core plug not exposed to mud filtrate (Figure 6b). This means that the mud exposed core plugs were less water-wet than the reference core plug.

Capillary Desaturation After Mild And Strong Cleaning

An atypical CDC was determined after methanol cleaning of the composite reservoir core (Figure 7). The same reservoir core was then prepared by cleaning with methanol/toluene, acetic acid and ethanol. The CDC profile was then as expected for water-wet rock where the residual oil at low capillary number is distributed as isolated droplets (Figure 7). This showed the importance of the type of cleaning procedure. When these measurements were carried out, the understanding was that sandstone rock should be water-wet. Since atypical CDC was measured after methanol cleaning, it was based on results presented by Garnes et al. [6] assumed that the reservoir core was contaminated by oil-based mud. During injection of acetic acid the mineral composition of the reservoir rock was probably altered, e.g. dissolution of carbonate minerals. Today many of the sandstone oil reservoirs are characterized as mixed-wet. In recent years it has been shown that atypical CDC can be determined for the wetting phase [5] and also for mixed-wet rocks [7].

DISCUSSION

All mud components should ideally be removed during preparation of reservoir core plugs. The main challenge is that the muds and mud filtrates contain many components. It has been shown in the present study that analysis of effluent samples during cleaning of core plugs can confirm that the mud components that are easiest to remove are removed, e.g. ions in water-based mud and emulsifiers in oil-based mud. If these components are still present in the rock, the rock is probably not representative. It has also earlier been reported that emulsifiers can adsorb onto the rock and thereby alter the wettability [8]. Emulsifiers will not give any colour to the effluent, but the effluent can be analysed for these components or IFT can be measured. If the reservoir rock has been invaded by water-based mud, it is important that the composition of brine in the rock is changed to FW composition. It has been shown in other studies that potassium can reduce the concentration of divalent cations onto clay surfaces and thereby alter the wettability to more water-wet [9, 10]. Differential pressure across the core plugs can't be used to confirm that mud contaminations have been removed, because low concentrations of such contamination will have minor effects on viscosity.

After cleaning, the rock can be crushed and analysed for mud components (e.g. by SEM) and oil residue (e.g. by analysing oil extracts on GC). These methods are destructive.

Often extra core plugs are cleaned and prepared in experimental programs, and the additional plugs can be analysed to confirm the quality of the cleaning. An alternative is to analyse cores/plugs after the SCAL- or EOR-experiments in the same way. It was not possible to identify bentonite clay by the used SEM method, but invasion of clay from water-based muds will increase the surface area. This can affect the established wettability conditions during aging with stock tank oil. The organoclay in oil-based muds are oil-wet, and invasion of this clay will also alter the wettability of the reservoir rock.

It is challenging to analyse for all the mud components, because the muds their filtrates contain many components of technical grade (i.e. standard set for quality is not established). If mud components are present, the question is to what extent do they affect the results. If several SCAL- or EOR-experiments have been carried out, it can be investigated whether the results depend on the amount of mud invasion in the different cores/plugs. The best chance will be to get as low mud invasion as possible during coring. Invasion will depend on the sampling conditions, mud design, and over balance used in the coring process, but will in general decrease with decreasing permeability.

The cleaning procedure for reservoir core plug can be improved by including chemical analyses. Details in the preparation procedure will depend on the composition of the rock, reservoir fluids and mud system. In the evaluation of the cleaning procedure for water-based muds, oil components with high molecular weight were found in the oil residue. The solvent cleaning was carried out at 60°C. It will probably be possible to remove these components more efficiently by cleaning the core plugs at higher temperatures. Cleaning at higher temperature will increase the diffusion rate and the solubility of the high molecular oil components. This is an example of how chemical analysis can be used to improve the core preparation procedure.

CONCLUSIONS

In evaluation of the cleaning procedure for high permeability sandstone reservoir core plugs with potential contamination by water-based mud, injection of several PV with SFW were required to change the brine composition in the core plugs back to SFW composition. Mud components were found by SEM-analysis to be present in cleaned reservoir rock, also after water flooding. The cleaned reservoir rock was water-wet, but mud components present in the rock affect the wettability conditions prepared by aging with crude oil. Cleaned reservoir rock was also found to contain oil components of high molecular weight. Slow release of emulsifiers from mud filtrate of oil-based muds was observed during cleaning of sandstone with STO injection. After this cleaning the core plugs exposed to mud filtrate were found to be less water-wet than reference core plug without exposure.

The measured CDC for sandstone reservoir rock with potential contamination with oil-based mud, was found to depend on the cleaning procedure. Atypical CDC was measured after methanol cleaning, and typical CDC was measured for water-wet rock after strong cleaning (methanol/toluene, acetic acid and ethanol). The strong cleaning probably altered the rock composition.

Mud components with the potential to affect the flow conditions should be removed during cleaning of reservoir core plugs, otherwise, ideally, these core plugs should not be used. In preparation of core plugs it is recommended to analyse effluent samples for mud components to confirm that they are removed, at least the easiest removable components. The cleaning procedure should be evaluated for the actual reservoir rock by analysing cleaned plugs for wettability and mud components. For some mud components, chemical analysis can be challenging because they are of technical grade, have similar structures as other mud components and are in complex mixtures. Important minerals should not be removed from the original reservoir rock during cleaning. It is recommended to analyse core plugs in experimental programs to investigate whether the presence of mud components may have affected the results.

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Table 1. Composition of SFW.

| Ion | Concentration (mg/l) |
|-------------------------------|----------------------|
| Na ⁺ | 16105.6 |
| K ⁺ | 278.0 |
| Mg ²⁺ | 581.0 |
| Ca ²⁺ | 2920.0 |
| Sr ²⁺ | 103.5 |
| Ba ²⁺ | 5.6 |
| Cl ⁻ | 31744.4 |
| NO ₃ ⁻ | 146.5 |
| SO ₄ ²⁻ | 281.1 |

Table 2. Elemental compositions (w%) of inlet, mid and outlet samples of cleaned reservoir core plug based on EDS-spectra.

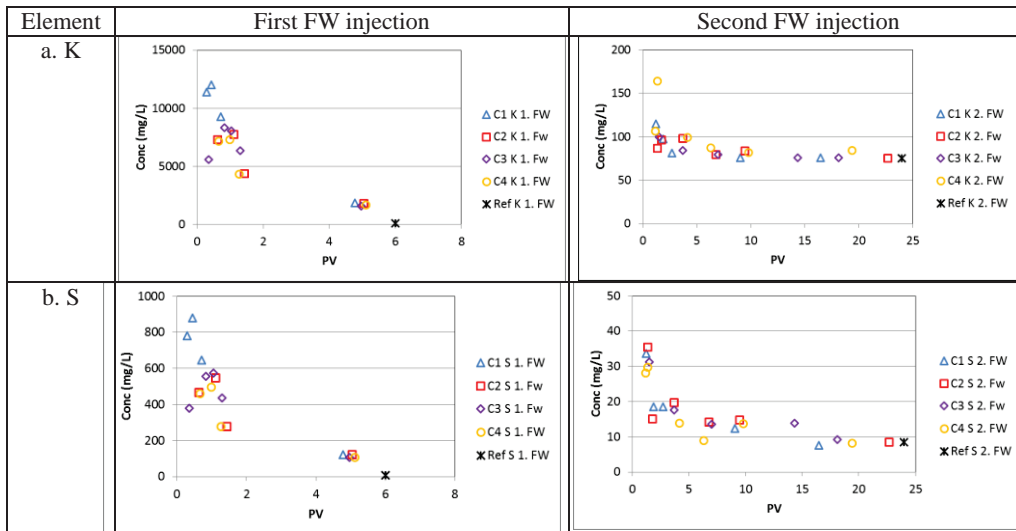
| Element | Inlet | Mid | Outlet |
|---------|-------|------|--------|
| O | 36.3 | 37.7 | 38.5 |
| Na | 1.2 | 0.6 | 0.4 |
| Mg | 0.1 | 0.1 | 0.2 |
| Al | 6.9 | 6.6 | 5.4 |
| Si | 45.5 | 43.6 | 45.2 |
| S | 1.0 | 0.9 | 1.0 |
| K | 3.8 | 5.3 | 4.0 |
| Ba | 3.7 | 3.5 | 3.5 |
| Fe | 1.5 | 1.8 | 1.8 |

Table 3. Amount of oil extracted from cleaned reservoir core plug.

| Sample id | Extracted material (mg/kg Rock) |
|-----------|---------------------------------|
| Inlet | 62 |
| Mid | 132 |
| Outlet | 604 |

Table 4. Less water-wet core plugs (by aging with STO) and exposed to mud filtrates with mineral and synthetic base oils (MFM and MFS).

| Step | Ref. core plug ke _o (S _{wi}) [mD] | MFM core plug ke _o (S _{wi}) [mD] | MFS core plug ke _o (S _{wi}) [mD] |
|---|--|---|---|
| After first aging with STO | 96 | 112 | 130 |
| After aging with mud filtrate (reference aged with STO) | ----- | 96 | 136 |
| After second aging STO | 99 | 119 | 144 |



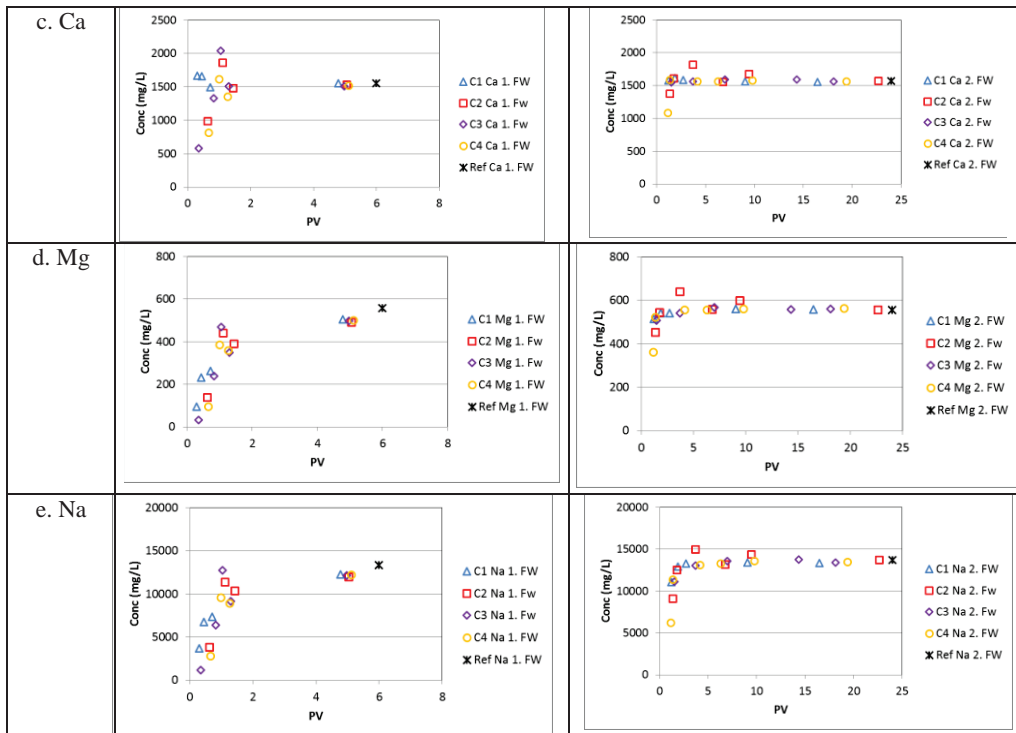
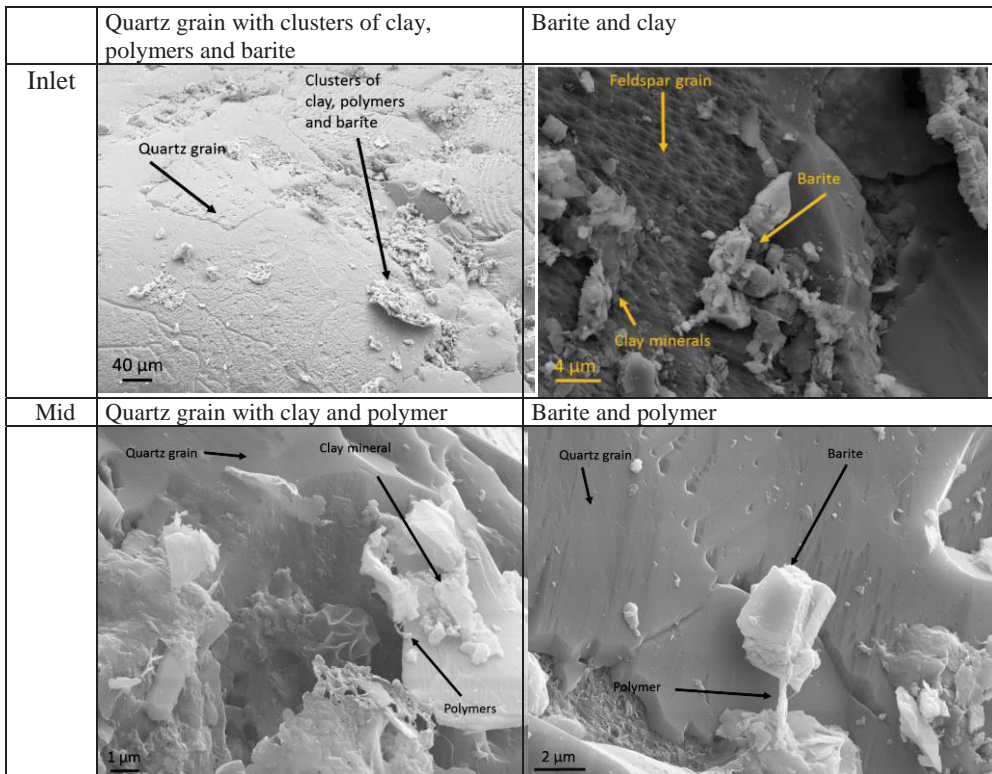


Figure 1. Effluent element concentrations during SFW injection before and after solvent cleaning of four core plugs.



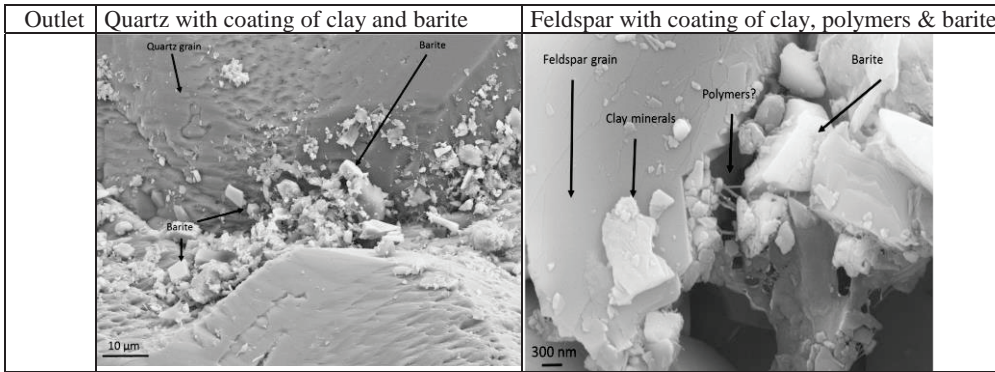


Figure 2. Examples of SEM-images of samples from cleaned reservoir core.

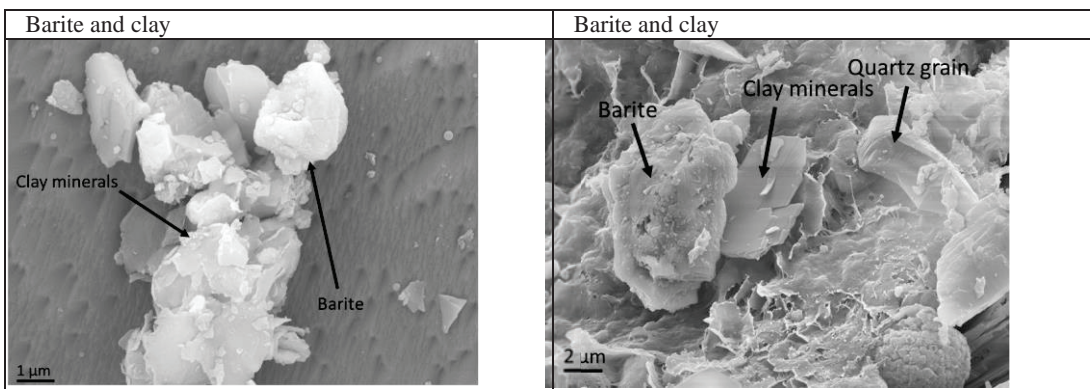


Figure 3. Examples of SEM-images of samples from water flooded reservoir core plugs.

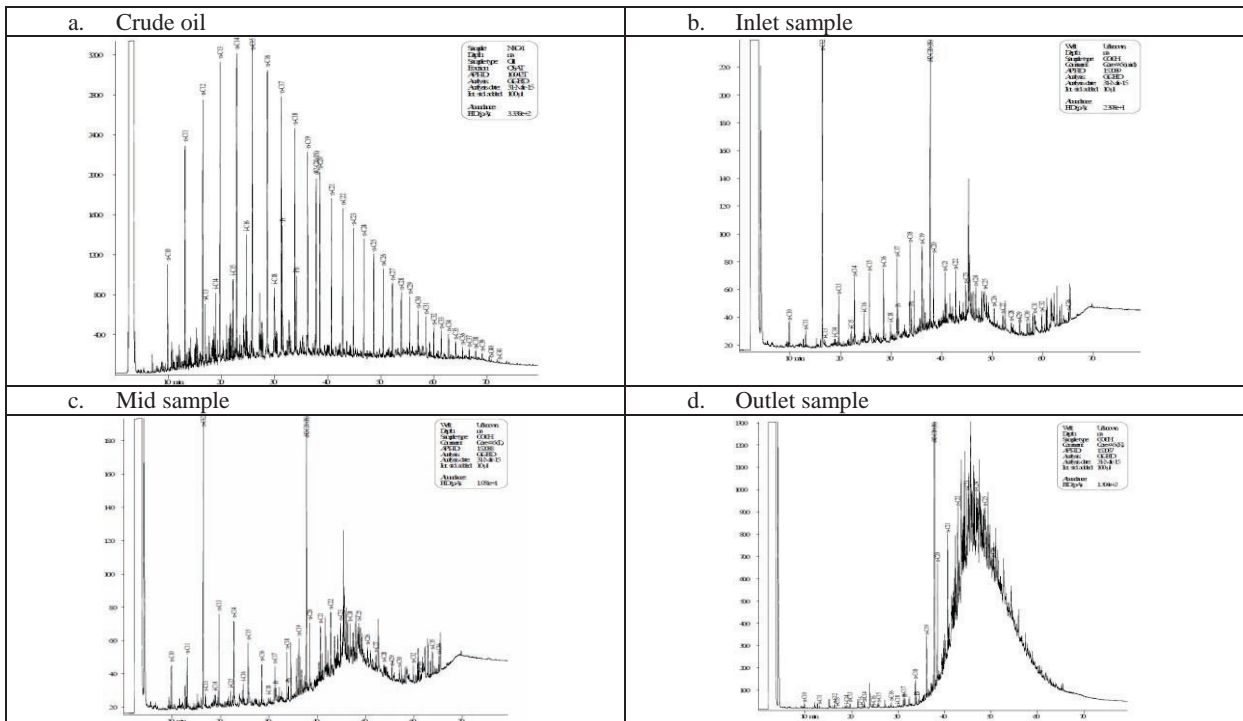


Figure 4. Gas chromatogram of crude oil and oil extracts from inlet, mid and outlet of cleaned reservoir core plug.

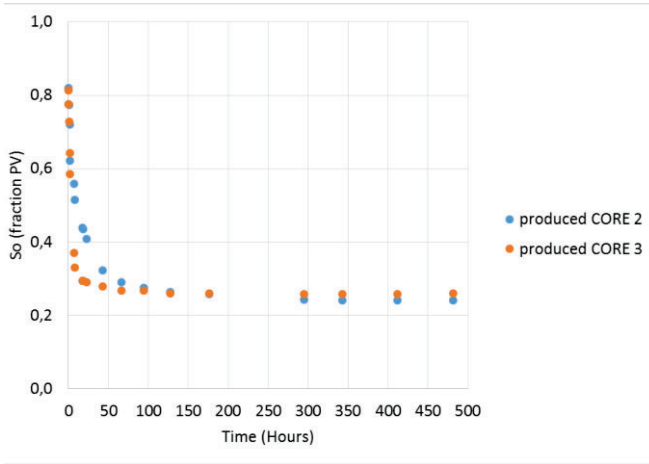


Figure 5. Oil saturation (S_o) as function of time during spontaneous imbibition of SFW into reservoir core plugs.

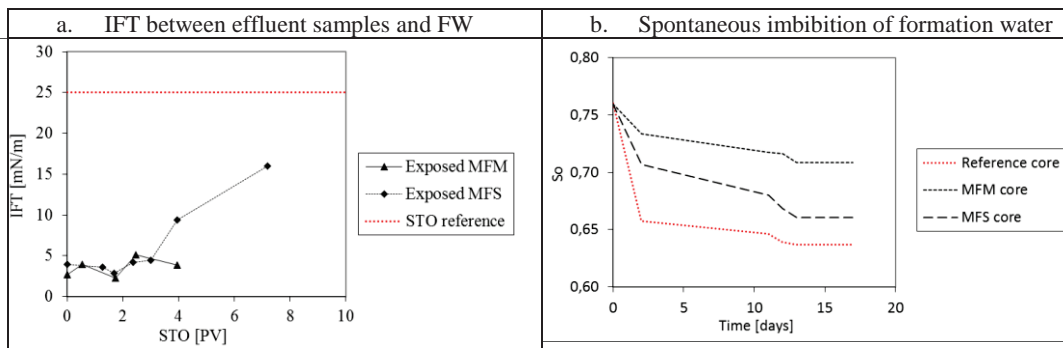


Figure 6. IFT between effluent samples and FW during soft cleaning by STO and the following spontaneous imbibition experiments with SFW. (MFM and MFS: Mud filtrates with mineral and synthetic base oils).

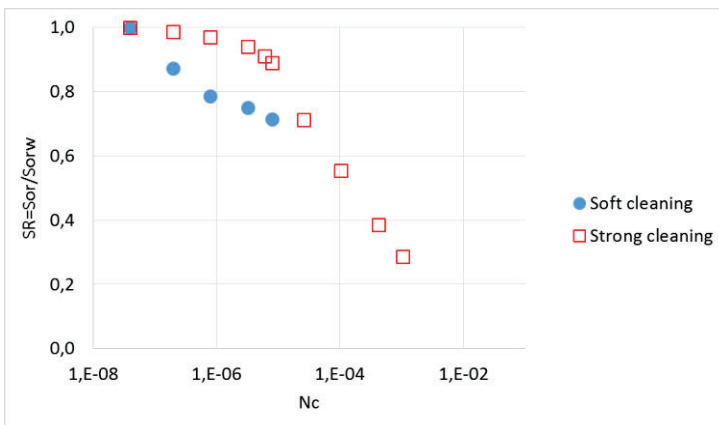


Figure 7. CDC, normalized residual saturation vs capillary number (S_{or}/S_{orw} vs N_c) after methanol cleaning (soft) and after cleaning with methanol/toluene, acetic acid and ethanol cleaning (strong) of reservoir core.