WETTABILITY AND PREDICTION OF OIL RECOVERY FROM RESERVOIRS DEVELOPED WITH MODERN DRILLING AND COMPLETION FLUIDS

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Project Objectives

The objectives of this project are:

1. to improve understanding of the wettability alteration of mixed-wet rocks that results from contact with the components of synthetic oil-based drilling and completion fluids formulated to meet the needs of arctic drilling;

2. to investigate cleaning methods to reverse the wettability alteration of mixed-wet cores caused by contact with these SBM components; and

3. to develop new approaches to restoration of wetting that will permit the use of cores drilled with SBM formulations for valid studies of reservoir properties.

Abstract

Exposure to crude oil in the presence of an initial brine saturation can render rocks mixed-wet. Subsequent exposure to components of synthetic oil-based drilling fluids can alter the wetting toward less water-wet or more oil-wet conditions. Mixing of the non-aromatic base oils used in synthetic oil-based muds (SBM) with an asphaltic crude oil can destabilize asphaltenes and make cores less water-wet. Wetting changes can also occur due to contact with the surfactants used in SBM formulations to emulsify water and make the rock cuttings oil-wet. Reservoir cores drilled with SBMs, therefore, show wetting properties much different from the reservoir wetting conditions, invalidating laboratory core analysis using SBM contaminated cores. Core cleaning is required in order to remove all the drilling mud contaminants. In theory, core wettability can then be restored to reservoir wetting conditions by exposure to brine and crude oil. The efficiency of core cleaning of SBM contaminated cores has been explored in this study.

A new core cleaning procedure was developed aimed to remove the adsorbed asphaltenes and emulsifiers from the contaminated Berea sandstone cores. Sodium hydroxide was introduced into the cleaning process in order to create a strongly alkaline condition. The high pH environment in the pore spaces changed the electrical charges of both basic and acidic functional groups, reducing the attractive interactions between adsorbing materials and the rock surface.

In cores, flow-through and extraction methods were investigated. The effectiveness of the cleaning procedure was assessed by spontaneous imbibition tests and Amott wettability measurements. Test results indicating that introduction of sodium hydroxide played a key role in removing adsorbed materials were confirmed by contact angle measurements on similarly treated mica surfaces. Cleaning of the contaminated cores reversed their wettability from oil-wet to strongly water-wet as demonstrated by spontaneous imbibition rates and Amott wettability indices.

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Cleaning Cores after Contamination with Synthetic Oil-based Mud Components

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Introduction

Drilling muds are used to lubricate drill bit and drill string, maintain formation pressure to prevent blowouts, and transport drilled cuttings from borehole to the surface. A great number of drilling muds have been developed to meet different drilling conditions. These drilling muds can be classified into three categories: water-based muds (WBMs), oil-based muds (OBMs) that often used diesel as a base oil, and synthetic oil-based muds in which diesel is replaced by a variety of base oils that meet environmental regulations. OBMs are usually employed to replace WBMs when water sensitive shale formations are being drilled. SBMs are frequently used for drilling in environmentally sensitive areas such as the Gulf of Mexico, the North Sea and Arctic regions where use of OBMs may pose serious environmental issues. While removal of aromatic compounds decreases toxicity of the drilling mud, it can create asphaltene stability problems that do not occur with diesel-based fluids.

During the drilling process, hydrostatic pressure in the borehole often exceeds that in the penetrated formation, so that drilling fluid invades some of the pore space of recovered core. Previous investigation (Zhang et al., 2004) indicated that displacement of crude oils with SBM base oils such as olefins tended to decrease the water-wet character of the tested cores even in the absence of added emulsifiers and oil-wetting surfactants. This wetting alteration was ascribed to surface precipitation of asphaltenes.

When drilling mud emulsifiers are involved, the emulsifiers can adsorb on the rock surface and further increase the oil-wetness of the tested cores. Measurements of imbibition rate as a function of emulsifier concentration showed that cores became less water-wet with increase in emulsifier concentration (Skalli et al., 2004). The wetting change may be further aggravated when the core is brought to the surface because of the loss of light ends or the deposition and oxidation of heavy ends (Wendel et al., 1985).

Change in wettability of the recovered reservoir cores affects special core analysis including capillary pressure, relative permeability, and waterflood recovery (Anderson, 1986, Morrow,1990), leading to unreliable reservoir evaluation and prediction of waterflood performance. One approach to using SBM contaminated cores is to clean the cores and restore to the original reservoir wetting conditions by re-exposure to reservoir fluids. The efficacy of cleaning processes has been studied for WBM and OBM-contaminated cores (e.g., Anderson, 1986; Cuiec, 1989), but studies of cleaning SBM-contaminated cores are limited (McCaffery et al., 2002; Skalli et al, 2004; Zhang et al., 2004).

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Gant and Anderson (1988) tested many common cleaning solvents and combinations of solvents for cleaning cores contaminated with invert emulsion oil-based muds. The best results in both sandstone and carbonate cores were achieved using a Dean-Stark extraction method with either a 1:1 mixture of toluene and methanol or the same 1:1 mixture to which 1% NH_4OH was added. Cleaning was judged by USBM wettability index measurements (Donaldson et al., 1969). The authors speculate that flow-through cleaning would be even more efficient than their extraction process with the same solvents.

Hirasaki et al. (1990) tested flow-through cleaning of reservoir cores with several sequences of solvents and solvent mixtures. Whether the cores were suspected of drilling fluid contamination and what kind of drilling fluid was used in the coring program were not specified. As a result of their tests, they recommended displacing oil with toluene or chloroform, followed by tetrahydrofuran (THF) to remove adsorbed asphaltenes and waxes. The THF can also adsorb, but is displaced along with water and salts by a final flush with methanol.

In this study, Berea sandstone cores were aged in either Gullfaks or Minnelusa crude oil to generate mixed-wet conditions. Mixed-wet cores were then exposed to a simulated SBM. For the simulated SBM, a base oil consisting of fatty acid esters that does not cause asphaltene precipitation was chosen. To that base oil were added two commercial drilling mud surfactant products, an emulsifier and a wetting agent. Wetting conditions were quantified by measurements of the rate of spontaneous imbibition and by Amott indices relating the amount of each fluid that imbibes spontaneously and the amount that can be moved in a forced displacement. In all cases, the mixed-wet cores became preferentially oil-wet upon contamination. Following SBM contamination, cores were cleaned by several techniques including a newly developed sequential strategy that incorporates strongly alkaline conditions.

Experimental Materials and Methods

Cores

Berea sandstone cores, 3.8 cm in diameter and 7.5 cm long, were used in all tests. Average core porosity was 17% and average air permeability was 75 md.

Crude oils

Two crude oils, Gullfaks from the North Sea and Minnelusa from Wyoming, were used to create Mixed-wet conditions in the Berea sandstone cores. These two crude oils have much different asphaltene contents and their selected properties are summarized in Table 1.

Table 1. Crude oil properties

Name	°API	RI at 20°C	RI at 60°C	n-C_7 asphaltenes (wt %)	Acid #	Base #	viscosity at 20°C (mPa s)
					mg KOH/g oil		
Gullfaks	27.1	1.4930	1.4761	0.4	0.24	1.19	16
Minnelusa	24.6	1.5143	1.4979	9.0	0.17	2.29	56

Brine

The aqueous solution used in the initial saturation of cores was selected to simulate the composition of sea water. This synthetic sea water (SSW) contained 28g/L NaCl, 0.94g/L KCl, 11.45g/L $MgCl_2 \cdot 6H_2O$, and 1.58g/L $CaCl_2 \cdot 2H_2O$.

Drilling mud formulation

The simplified synthetic drilling fluid was prepared by mixing Petrofree LV with 0.37vol% Le Supermul and 0.24vol% Le Mul unless otherwise specified. Properties of the base oil and the emulsifiers are summarized in Table2. The emulsifier concentrations were one-tenth of the maximum concentrations recommended for use in drilling industry. Petrofree LV is composed of fatty acid esters. Among the two emulsifiers, Le Supermul is mainly used as a wetting agent and Le Mul is mainly used as an emulsion stabilizer.

Table 2. Properties of base oil and emulsifiers

Trade name	Density at 20°C (g/ml)	Viscosity at 20°C (cP)	Material description
Petrofree LV	0.8617	3.86	fatty acid esters
Le Supermul	0.92	200-300	polyaminated fatty acids
Le Mul	0.92	1550-1750	polyaminated fatty acids plus oxidized tall oil fatty acids

Contact angle measurements

Water-advancing and water-receding contact angles were measured with decane as the probe oil on mica surfaces after exposure of the clean mica to brine, crude oil, SBM components, and cleaning solvents, using the same fluids as those used in the core tests. Treatment and measurement techniques have been described in detail previously (Liu and Buckley, 1997, 1999; Skalli et al., 2004).

Preparation of contaminated cores

Core samples at initial water and oil saturations were aged in either Gullfaks oil or Minnelusa oil at 75^{o}C for 10 days. After injection of 5 PV of the synthetic drilling fluid, the cores were left in the fluid overnight at 50^{o}C. The properties of the treated cores including Amott wettability indices are listed in Table 3.

Table 3. Properties of the oil and SBM-treated cores

Core	kg, md	Swi, %PV	Aging oil	Amott index
C4-1	63	25.2	Minnelusa	-
C4-10	75	25.8	Gullfaks	-0.33
C4-11	63	25.2	Gullfaks	-0.40
C4-14	69	25.5	Gullfaks	-0.46
C4-15	74	25.8	Minnelusa	-0.61
C4-16	74	24.6	Gullfaks	-0.32
C4-17	75	25.8	Minnelusa	-0.53
C4-19	61	25.7	no crude oil	-0.40
C4-21	75	25.4	no crude oil	-0.44

Cleaning methods

Two methods, flow through and extraction, were tested to compare their cleaning efficiency. In the flow-through method, contaminated cores were mounted in a Hassler cell and flushed at a flow rate of 3 ft/day with 10 PV of each solvent at 50^{o}C. The direction of flow was reversed midway through the flushing process for each solvent.

In cleaning tests by the second method, a Soxhlet extraction apparatus was used to flush the cores for 24 hours with 300 ml of each solvent. Cores were inverted after 12 hours to facilitate contact of solvent throughout the length of each core. If the extracting toluene became very dark, indicating that a significant amount of material was removed by toluene, this step was repeated with fresh toluene before introducing other solvents. After cleaning, the core was allowed to dry at ambient conditions for about 5 hours, followed by drying in an oven at 110^{o}C for 24 hours.

Sequence of cleaning solvents

For mixed-wet cores, wettability alteration to more oil-wet conditions can occur if connate water is disturbed while crude oil is in the core (Anderson, 1986). If toluene is used to remove crude oil, water is also removed because it has significant solubility in hot toluene. Refluxing in toluene has an even greater potential for removing water because at the boiling point of toluene (110.8°C) water is vaporized. The choice of a solvent to remove bulk crude oil is further complicated by the potential for wetting changes if asphaltenes are destabilized. In this work we selected cyclohexane, which in most cases should not precipitate asphaltenes, as the first solvent. Solubility of water is low in cyclohexane, and its boiling temperature (80.7°C) is below the boiling point of water.

Once oil is removed, the subsequent solvents, toluene, isopropanol, and 1% wt/vol NaOH dissolved in isopropanol, were chosen for their ability to dissolve asphaltenes, remove water, and to cause polar material—from either oil or SBM components—to desorb from pore surfaces. Three step treatments used cyclohexane followed by toluene, then by isopropanol. An even more rigorous cleaning was attempted using a five-step or six-step sequence including 1% wt/vol NaOH in isopropanol. Some single-step tests using the mixture recommended by Gant and Anderson (1988) of 49.5% toluene, 49.5% methanol, and 1% wt/vol NH_4OH, were included in the extraction series for comparison to the multi-step processes introduced in this work. The solvent sequence details, identified by the number of steps involved are summarized in Table 4. Note that the toluene step may be repeated in any of the multi-step treatments.

Table 4. Solvents and sequences in which they are applied in single and multi-step cleaning

Number of steps	**Solvents and sequence**
1	a mixture of 49.5% toluene + 49.5% MeOH + 1% wt/vol NH_4OH
3	c-C_6 → toluene → IPA
5	c-C_6 → toluene → IPA → 1% wt/vol NaOH in IPA → IPA
6	c-C_6 → toluene → IPA → 1% NaOH in IPA → 1% wt/vol KCl in H_2O → MeOH

Imbibition tests

The rate of spontaneous imbibition of water was determined, based on oil recovery as a function of time. Imbibition rates are reported in terms of dimensionless time, t_D, which is defined as:

$$t_D = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{(\mu_o \mu_w)^{1/2}}\frac{1}{L_c{}^2}$$

where t is the actual imbibition time, k is permeability, ϕ is porosity, σ is interfacial tension between oil and water, μ_w and μ_o are viscosities of water and oil, respectively, and L_c is the characteristic length of the core (Ma et al., 1997). t_D is scaled to account for differences in core petrophysical properties and geometry as well as fluid properties except for core wetting preference. Because core wettability is not included in this correlation group, differences in core wettability are indicated by comparing the scaled rates of imbibition. Amott indices (Amott, 1959) were measured for the same cores using forced displacements in a Hassler cell following spontaneous imbibition of water and spontaneous imbibition of oil.

Results and Discussion

Results of core cleaning by the various techniques described above are summarized in Table 5.

Table 5. Summary of core cleaning results

Core	Cleaning process	change in k_g (md)	I_{AH} after cleaning
C4-1	1	-15	0.66
C4-14	3	-26	-
C4-15	5	-24	0.93
C4-16	3*	-48	0.33
C4-19	1	-25	0.82
C4-21	6	-38	0.89

* Flow-through cleaning (all others were cleaned by extraction

Three-step treatments with cyclohexane, toluene, and isopropanol

Mixed-wet cores C4-14 and C4-16 were preferentially oil-wet after exposure to SBM (Table 3). Neither core imbibed any water. Figure 1 shows the results of the three-step cleaning procedures applied with both flow-through and Soxhlet extraction methods. The top curve in this figure is the very strongly water-wet (VSWW) reference curve obtained from a core that was treated only with brine and purified mineral oil with an initial water saturation of about 25 %. After the three-step cleaning sequence, whether applied in flow-through or extraction mode, the cores spontaneously imbibe water, indicating a return to preferentially water-wet conditions. The rate and extent of imbibition, however, are less than the VSWW reference state, suggesting the need for a more aggressive cleaning strategy for cores exposed to these surfactants. Although in this case the two application methods gave similar results, it should be noted that lower permeability cores might not be cleaned as well by extraction as by a flow-through technique.

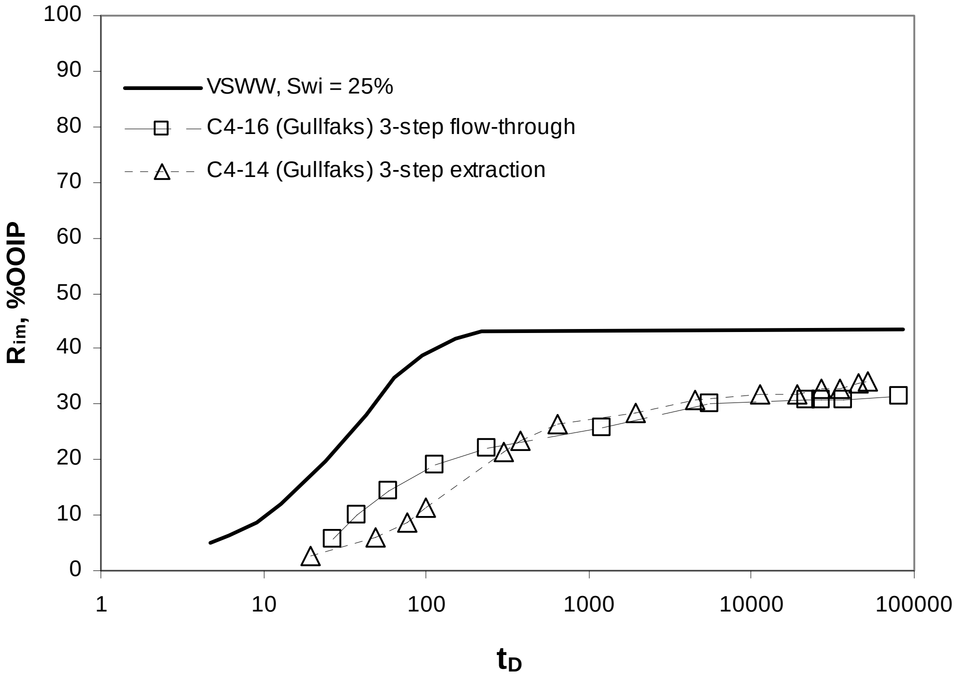

Figure 1. Cores cleaned by three-step solvent sequence of cyclohexane, toluene, and isopropanol are weakly water-wet. There is little difference between flow-through and extraction applications of the solvents.

Five-step treatments with cyclohexane, toluene, isopropanol, 1% NaOH in isopropanol, and isopropanol

A more rigorous cleaning procedure was tested in extraction mode with SBM contaminated core C4-15, for which the Amott index indicated the most oil-wet conditions of any of the contaminated cores. Figure 2 shows the results of the cleaning process both in terms of imbibition rate and Amott number. Initial imbibition of water still trails that of the strongly water-wet core, but the amount imbibed is higher and the Amott index is 0.92. Sodium hydroxide appears to play an important role in removing drilling mud contaminants. It is possible that NaOH might alter the surface chemistry of the core but previous investigation (Pashley, 1978) indicated that the effect would not be significant.

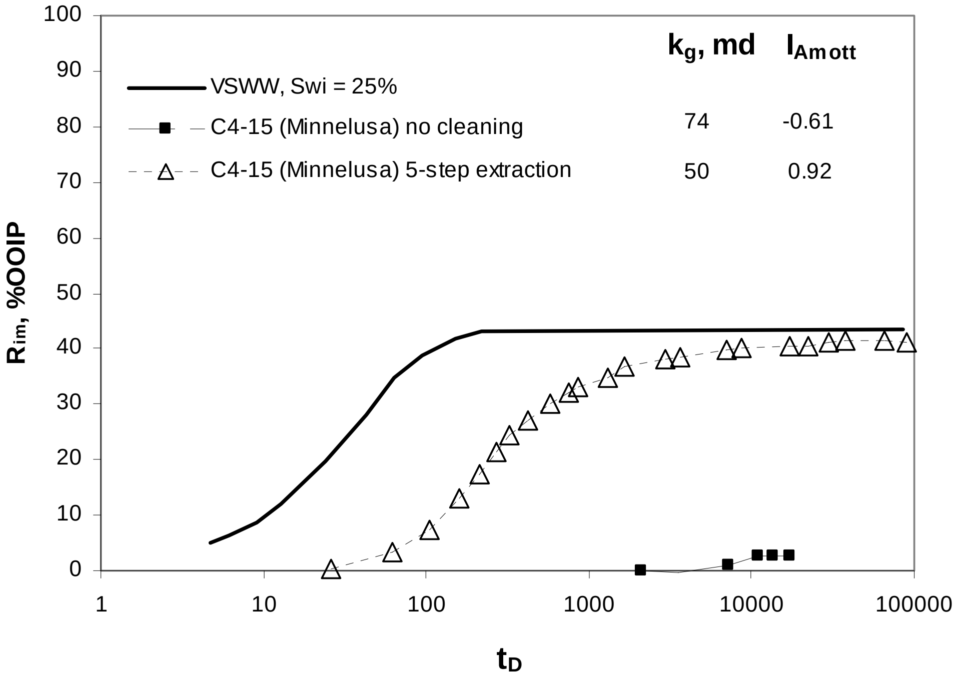

Figure 2. Comparison of imbibition rates before and after cleaning by the five-step extraction process.

A similar solvent sequence was used to clean mica that had been exposed to SSW, Minnelusa crude oil, and the synthetic SBM. Results are summarized in Fig. 3. Mica was exposed first to SSW, then to Minnelusa crude oil either at ambient conditions for 21 days or at 75°C for 10 days. After rinsing briefly with toluene, contact angles were measured with decane and water. Subsequent exposure to synthetic SBM made the wetting of the mica surfaces neutral. Soaking in cyclohexane and toluene at room temperature reduced contact angles only slightly, whereas soaking in a 1% wt/vol NaOH solution in IPA returned the surfaces to a preferentially water-wet condition.

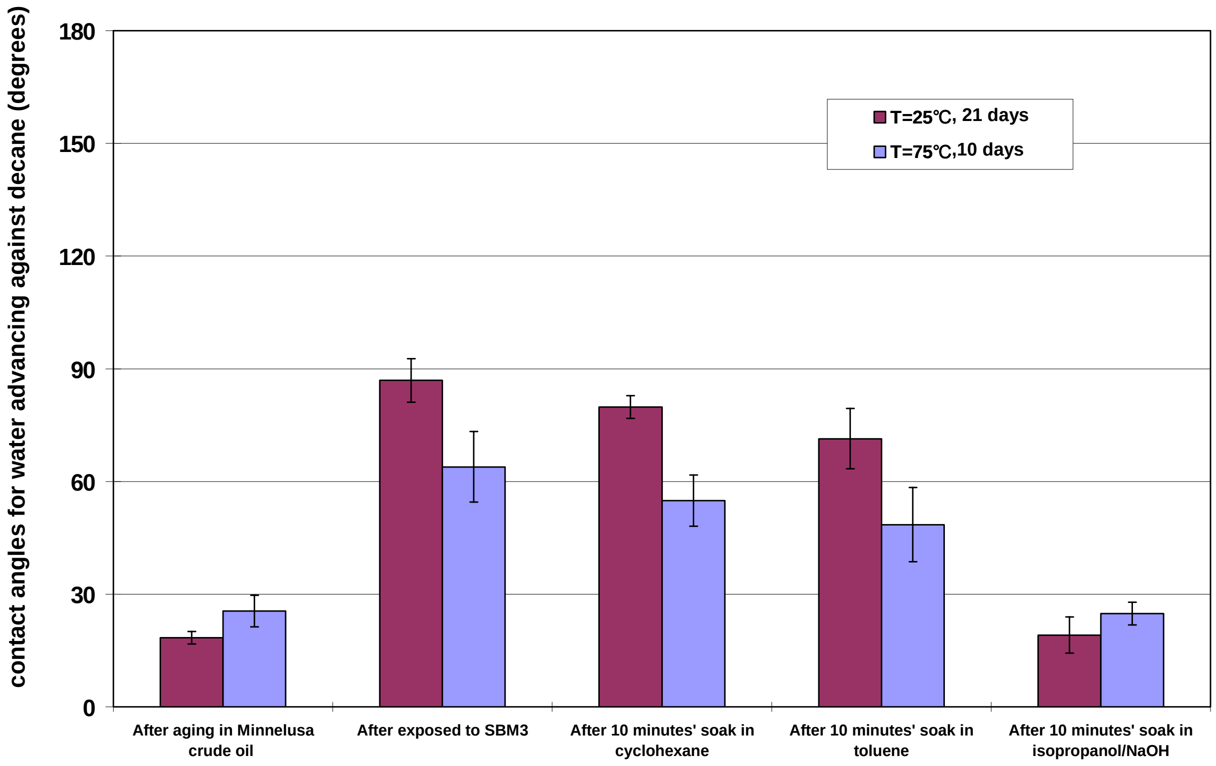

Figure 3. Comparison of imbibition rates before and after cleaning by the five-step extraction process.

Effect of crude oil

Effectiveness of extraction processes that included a high pH step was compared for two cores, one of which was treated with crude oil before exposure to the synthetic SBM. The other core was exposed to SBM only. The extraction processes were adapted for Core 4-21 after the 1% wt/vol NaCl in IPA step to include an aqueous flush followed by methanol because salt crystals were observed. Cleaning was effective for both cores, as indicated by Amott indices of 0.89 and 0.93, but initial rate of imbibition was faster for the core that had not been exposed to crude oil, as shown in Fig. 4.

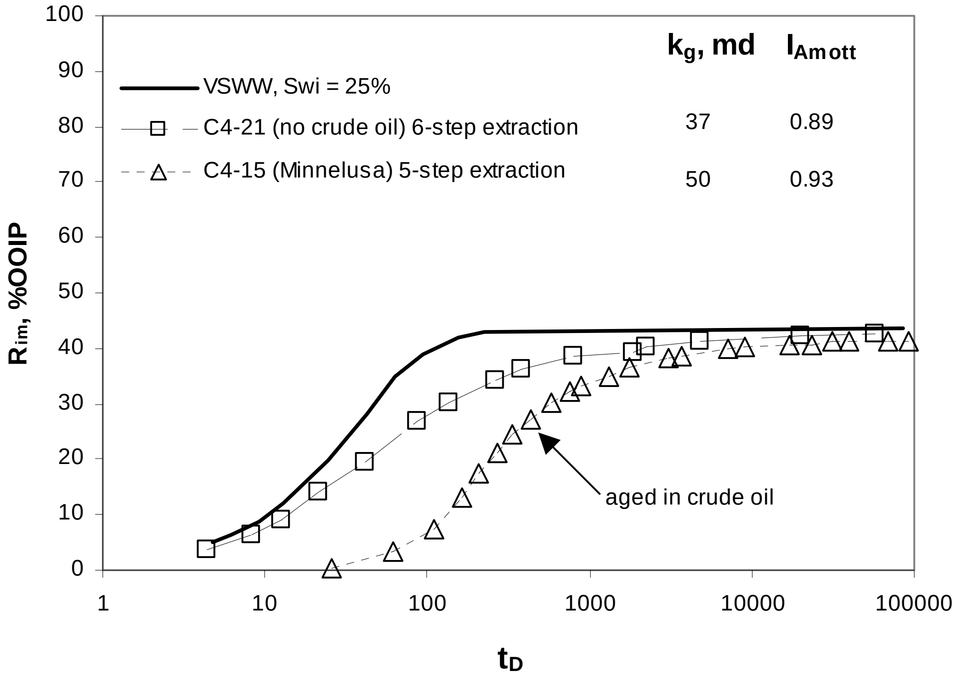

Figure 4. Cleaning of SBM-contaminated cores with a sequential process including a high-pH step is efficient for cores whether they were very strongly water-wet or mixed-wet before exposure to SBM.

Comparisons to single-step extraction

The chemistry of the solvents chosen for this study is similar to those recommended by Gant and Anderson (1998), but there are some significant differences in the specific choices of solvents, in their sequential method of application, and in the cleaning results obtained for SBM-contaminated cores. Figure 5 compares rates of imbibition and Amott indices for cleaning of SBM contaminated cores that had not been exposed to crude oil; Fig. 6 shows similar results for initially mixed-wet cores. In both cases, the multi-step cleaning procedure was significantly more effective than cleaning in a single-step using a mixture of solvents.

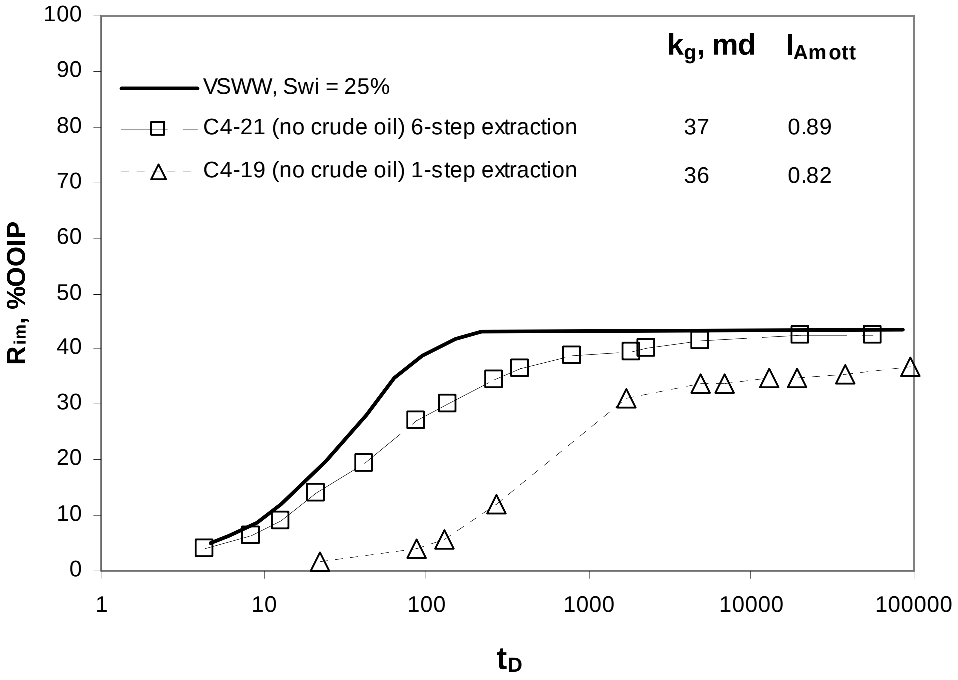

Figure 5. Comparison of cleaning SBM-contaminated cores by single and multi-step processes. Cores were very strongly water-wet before exposure to SBM.

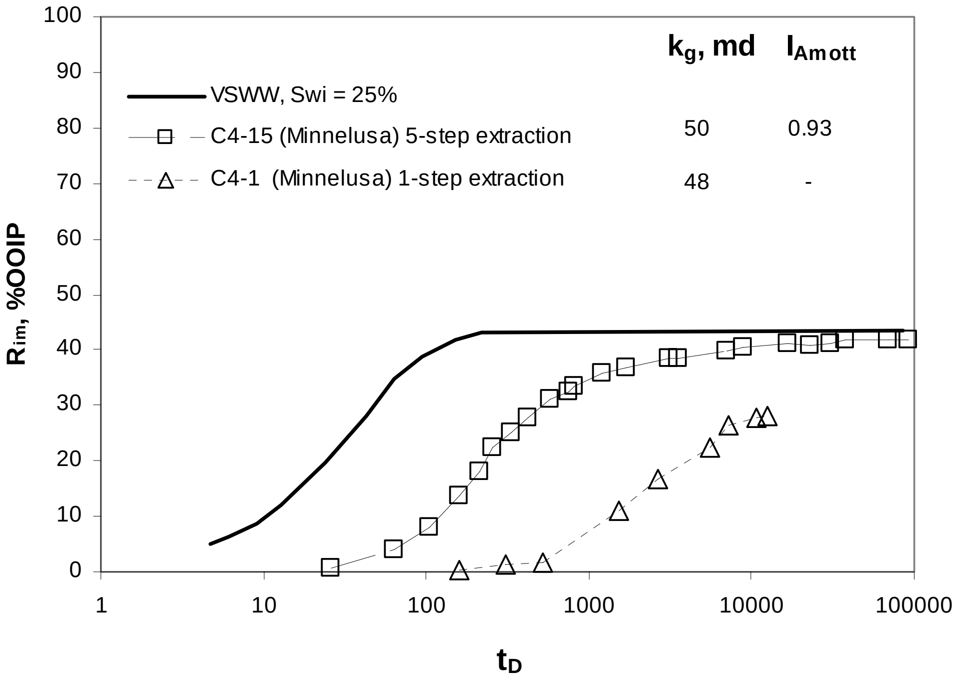

Figure 6. Comparison of cleaning SBM-contaminated cores by single and multi-step processes. Cores were mixed-wet before exposure to SBM.

Conclusions

1. Exposure to synthetic drilling fluid changed the wettability of Berea sandstone cores from their original strongly water-wet condition to oil-wet. Adsorption of emulsifiers and wetting agents added to the synthetic base oil are the major mechanisms for the wettability alteration.

2. Little difference was discerned between extractive and flow-through applications of the same solvent sequences.

3. In tests with different sequences of solvents, those that included sodium hydroxide were significantly more effective in removing drilling mud contaminants.

4. The new sequential core cleaning procedure including a high pH step was more effective in removing the wettability alteration materials from the rock surface than mixtures of similar materials, applied in a single step. The core cleaned with the solvent sequence that included NaOH showed very strong water-wetness, comparable to the uncontaminated cores.

Nomenclature

k - permeability, md
L_c - characteristic length
S_{wi} - initial water saturation, PV%
t - imbibition time, min
t_D - dimensionless time
T_a - aging temperature, ^oC
T_f - flooding temperature, ^oC
T_m - measurement temperature, ^oC
ϕ - porosity
μ_w - viscosity of water, cp
μ_o - viscosity of oil, cp
σ - interfacial tension, mN/m

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