WETTABILITY RESTORATION IN CORES CONTAMINATED BY FATTY ACID EMULSIFIERS

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ABSTRACT

A special core cleaning method has been developed for removing oil-based mud contamination from core plugs obtained from the Terra Nova field, offshore Newfoundland. The oil-based mud used to cut the core contained fatty acid emulsifiers, including oleic and linoleic acids. These compounds can polymerize, and also adsorb strongly on carbonate minerals, which are present as cement in the sandstone core material.

The core cleaning method was developed to establish a water-wet state in reservoir core that could not be cleaned effectively by a typical sequence of strong solvents. The effectiveness of various flow-through cleaning sequences was judged by measuring the rate of spontaneous imbibition using brine and a pure hydrocarbon. This is a rapid method that can be used easily on a large number of samples. The resultant cleaning method consisted of an 11-step treatment with both solvents and an aqueous alkaline solution. Potassium hydroxide (KOH) was found to be less damaging to permeability than sodium hydroxide. Following treatment with KOH, large volumes of brine throughput were required to return the core effluent to a neutral pH without using buffers (which might have also changed wettability).

The specially-cleaned core could then be aged to restore the *in situ* reservoir wettability. Ultimately this allowed representative special core analysis data to be acquired. Relative permeability data obtained using a composite core cleaned with the 11-step method and restored to reservoir wettability resembles relative permeability data obtained on core that had not been contaminated with oil-based mud.

INTRODUCTION

Rock properties, such as capillary pressure, relative permeability, and saturation exponent, depend on the distribution of water and oil in the pore space. In order for laboratory measurements to represent conditions in the reservoir, it is necessary for the pore-level distribution of the fluids and the wettability to be the same in the laboratory as in the reservoir. Most reservoir rock is believed to be in a mixed-wet state, i.e. neither completely water-wet nor completely oil-wet. Mixed wettability in the reservoir often results from the surface-active molecules in the crude oil adsorbing onto sand grains over

time. This mechanism is explained in detail by Kovscek *et al*. (1993), and is consistent with published data (Jadhunandan, 1995) and in-house core analysis experience.
In the laboratory, the reservoir wettability of cores usually can be restored by duplicating the process that established the wettability in the reservoir (Wang, 1994). This involves (a) establishing a water-wet state by solvent cleaning, (b) establishing saturations representative of the reservoir, or more precisely, a representative pore-level distribution of water and oil, and (c) aging in the presence of a high saturation of crude oil. Six weeks of aging is common industry practice, and numerous studies have shown that a stable wettability is achieved in this amount of time or less (Wendel *et al*., 1987 and Cuiec, 1991).

The first step in wettability restoration removes any contaminants from the rock mineral surfaces, and establishes a water-wet condition. A clean mineral surface is indicated by a water-wet condition since clean silica and calcite are strongly water-wet.   At ExxonMobil, miscible flow-through cleaning with a solvent sequence, often at elevated temperature, has been found to successfully establish a water-wet state in all previous cases except one in which the core contained pyrobitumen. The typical solvent sequence is similar to that proposed by Wang (1994) and is given in Table 1. However, this solvent sequence failed to establish a water-wet state in Terra Nova core material. Further work with Terra Nova core cut with a water-based mud indicated that the failure of the cleaning method was associated with the drilling mud, not with inherent properties of the crude oil-brine-rock system. Drilling records indicated that most of the wells had been cored with oil-based mud containing fatty acid emulsifiers.

BACKGROUND
Overview of the Terra Nova Field
The Terra Nova oil field is situated on the Grand Banks, about 350 km east-southeast of the city of St. John's in the Canadian province of Newfoundland and Labrador (Figure 1). Terra Nova is the second largest oil field discovered to date in the Jeanne d' Arc basin with estimated final oil production of 440 million bbls. Partner companies are Petro-Canada (Operator), ExxonMobil, Norsk Hydro, Husky Energy, Murphy Oil, Mosbacher, and Chevron Canada.

The field was discovered in 1984 at a water depth of about 95m. The reservoirs are located in the Upper Jurassic Jeanne d'Arc sandstone formation at 3,200-3,600 m below sea level. The first phase of development drilling occurred in 2000-2001. This included an extensive coring program, which provided most of the core material for the work reported here. First oil was produced on January 20, 2002. There are currently 27 wells in operation in the field; 16 oil producers, 8 water injectors and 3 gas injectors. In general, the Terra Nova reservoirs are highly productive, with some wells initially producing up to 40,000 bopd.

The oil is light, 33-37 deg API, with a solution GOR of 750-1000 scf/stb. Net pay of completed wells is typically 60-350 ft with field wide average porosity of 19% and

permeability 1,000 mD. The initial water saturation in the oil zone varies between 5% and 40% with a calculated average water saturation of 12%.

Reservoir rock ranges from very-fine sandstones to cobble conglomerates. Extensive chemical diagenesis has affected the reservoir intervals at Terra Nova. The more important aspects of chemical diagenesis include:

- precipitation of dolomite cement (due to mixing of seawater and freshwater at the time of deposition)
- precipitation of calcite cement (after significant burial had occurred)
- formation of quartz overgrowths

Figure 2 is a thin section image from a core sample, showing dolomite and calcite cements.

Wettability Alteration from Oil-based Drilling Fluids

Oil-based drilling fluids have been shown to alter rock minerals to an oil-wet or mixed-wet state (Anderson (1986), Ballard and Dawe (1988), and Gant and Anderson (1988)). Emulsifiers and surfactants included in these fluids, even at low concentrations, have been shown to be responsible for the change in wettability (Menezes *et al*. (1989), Yan *et al*. (1993), Thomas *et al*., (1984), and Tong and Morrow (2006)).

Drilling mud reports indicated that the Terra Nova coring fluids contained fatty acid emulsifiers, specifically oleic acid and linoleic acid. Both are carboxylic acids containing unsaturated C_{18} chains. They are known to polymerize under some conditions, and to adsorb on carbonate minerals, such as those in Terra Nova rock. Both mechanisms have the potential to prevent the core material from being cleaned to a water-wet state. Adsorption is reported to be stronger on carbonates than on siliceous minerals. This was recently demonstrated in regard to reservoir rock (Rezaei Gomari *et al*., 2006). However, as early as 1938, oleic acid was reported to be useful in separating quarried calcite from silica (Crago, 1938). The role of adsorbed acids in inhibiting diagenesis of reservoir rock has also been reported (Thomas *et al*., 1993).

While much literature exists about the contamination of wettability by oil-based drilling mud additives, fewer studies have focused on removing the contamination and restoring wettability. In work similar to that reported here, (Zhang *et al*., 2006), an alkaline solution was reported to be effective in cleaning contaminated Berea sandstone. Cuiec (1975) tested various solvents of an acidic or basic nature and observed that solvents of an acidic nature were more effective at cleaning sandstones, and basic solvents more effective at cleaning carbonate. In a study by Gant and Anderson (1988), a 49.5% methanol, 49.5% toluene, and 1% ammonium hydroxide solution was the best solvent for cleaning both Berea sandstone and Guelph dolomite core that had been contaminated with an oil-based mud containing fatty acids. However, they concluded that a cleaning method for core contaminated with drilling mud additives was dependent on the particular additives and core mineralogy. Wendel *et al*. (1987) studied the effectiveness of various solvent/solvent combinations on removing drilling-mud surfactants from contaminated Berea and Hutton cores.

They showed that a three-step method consisting of Dean-Stark extraction sequentially with toluene, glacial acetic acid, and ethanol cleaned contaminated sandstones to a water-wet state. However, they acknowledged that this method was not appropriate for core containing carbonate minerals, which can be dissolved by the glacial acetic acid.

The scope of work for the Terra Nova SCAL plugs called for solvent cleaning and wettability restoration, in preparation for relative permeability and capillary pressure measurements. Spontaneous imbibition tests were conducted to confirm that the expected behavior was observed. However, it was found that the standard strong-solvent cleaning failed to establish a strongly water-wet condition. Aging from this condition would probably not return the core to its original wettability state. In contrast, the standard strong-solvent cleaning was successful on plugs from the Terra Nova aquifer that had been cut with a water-based mud. This provided evidence that the cleaning difficulty was not inherent to the rock itself. Various solvent sequences were examined in developing a method for cleaning the Terra Nova core material in preparation for restoring it back to its *in situ* wettability state.

PROCEDURES
Core Material
The core material used for this work was obtained from six wells in the Terra Nova field. Five of the wells had been cored in 2000-2001, using oil-based mud containing fatty-acid emulsifiers and other additives. In 2004, 1½-inch diameter core plugs were cut from preserved intervals of whole core using synthetic formation brine. The core plugs were initially subjected to several days of Dean Stark extraction, followed by drying and measurements of approximate porosity and permeability to be used for plug selection. Although Dean Stark extraction is known to change rock wettability, it was considered justified in this case because the wettability had already been altered by the oil-based drilling mud. Wettability restoration, consisting of strong-solvent cleaning and aging with crude oil, was planned to reverse the effects of both the mud filtrate and extraction.

An earlier well had been cored in the aquifer in 1984 using a water-based mud containing no fatty acid emulsifiers. Preserved plugs from this well were available, but most appeared to be dry when open and inspected. This core material was considered to be a reference, for comparison with the oil-based mud drilled cores.

Test Fluids
Properties of the oil and brine at test conditions are given in Table 2.

Both live (gas-saturated) and dead (gas-free) crude oil were used in the work reported here. Both were obtained from a field oil sample taken upstream of chemical treatment points, and protected from oxygen exposure. Dead crude oil was prepared by drawing a partial vacuum (4 psia at 150°F). It was used for wettability restoration and for a limited number of spontaneous imbibition tests. Live crude oil, used for measuring relative

permeability, was prepared by adding gases to bring the composition of the oil back to that measured in a PVT study on a downhole oil sample.

Synthetic reservoir brine was formulated to match the composition measured on samples from the field and included 71,872 ppm of dissolved solids (67,600 ppm NaCl; 3,174 ppm $CaCl_2$; 628 ppm $MgCl_2$ and 470 ppm KCl). Sulfate and bicarbonate were omitted from the brine to avoid potential precipitation. In the steady-state relative permeability tests, this brine contained dissolved gases, as a result of contact with live crude oil. (The partially gas-depleted oil was later replaced with fresh live oil to bring it back to the *in situ* composition.)

Miscible Flow-Through Cleaning
Each of the solvent test sequences was performed using miscible flow-through cleaning. The core plugs were individually mounted in coreholders with a triaxial net confining stress of 1000 psig. For cleaning at elevated temperature, the cores were first heated to 150^oF in an oven. Each of the cleaning fluids was then flowed through the core at a rate no greater than 2 cc/min, with applied back pressure. For the steps in which brine was flowed to reduce the pH of the effluent stream to 7.0, up to 100 pore volumes throughput were required, using a slower rate and soaking periods.

Establishment of Irreducible Water Saturation
Irreducible water saturation was established by centrifuging the plugs at a capillary pressure similar to that in the reservoir. The plugs were stacked on "pedestals" of core material in order to achieve a more uniform saturation. This forces the region of high water saturation at the core outlet to be in the pedestal, not the plug itself.

Method for Assessing Wettability
In order to assess rock wettability as the core cleaning method was developed, approximately 40 spontaneous imbibition tests were conducted. In most cases, the tests were conducted at room temperature, using a pure hydrocarbon as the oil phase (99.9% tetradecane). Following each cleaning trial and establishment of irreducible water saturation, the oil phase was flowed through the plugs to establish a high oil saturation. The plugs were then loaded into imbibition cells with no confining stress and submerged in brine. Measurements were made of the volume of oil displaced from the plugs by spontaneous imbibition of brine as a function of time.

The degree of water-wetness was judged qualitatively by the rate and final amount of oil collected. These were compared with two references:
- water-wet Berea sandstone (outcrop rock cleaned with strong solvents)
- Terra Nova core plug cleaned only by Dean Stark extraction

A third reference was obtained after the core cleaning process had been developed:
- Terra Nova aquifer core, cut with water-based mud and cleaned with strong solvents.

Reservoir Condition Steady-State Relative Permeability
Steady-state water-oil relative permeability measurements were performed on composite cores constructed of several reservoir plugs of matched properties. The measurements were performed with live crude oil and synthetic brine at reservoir conditions of temperature (205°F), pressure (4500 psig), and net confining stress (3700 psi).

Aging at High Oil Saturation
To ensure that samples tested were of representative reservoir wettability, the plugs were aged in reservoir crude oil at irreducible water saturation at the reservoir temperature of 205°F. After centrifuging to irreducible water saturation, the plugs were mounted in coreholders end to end to form composite cores with 3700 psi applied net confining stress. The composite was heated to the aging temperature and dead oil was metered in while maintaining the appropriate stress. The composites were then aged for at least 6 weeks, occasionally being flushed with fresh dead crude oil.

Steady-State Test Procedure
Prior to the relative permeability tests, the dead crude oil used for aging was displaced with live crude oil and the effective permeability to oil was measured. The relative permeability tests were performed by pumping water and oil through the composite cores at total flow rates of 2-4 cc/min. Water saturation was determined by material balance using oil and brine volumes in a calibrated acoustic separator. The separator and pressure drop were monitored continuously. When both stabilized, the water fractional flow was increased to the next value. The final saturations were confirmed by vacuum distillation.

RESULTS
Cleaning Core Plugs to a Water-Wet Condition
The spontaneous imbibition results of two reference cores are shown in Figure 3. The data are shown on the basis of dimensionless time described by Zhang *et al*. (1996). The dimensionless time adjusts for the combined effects of permeability, fluid viscosity, sample size, and other variables. For the cases reported in this and subsequent figures, these variables had similar values, and the conversion to dimensionless time does not affect the appearance of the imbibition plots.

The spontaneous imbibition curve for clean Berea sandstone provides a strongly water-wet reference. Spontaneous imbibition is rapid and the plug imbibes a total of approximately 40% PV. The other reference is a Terra Nova reservoir core cleaned only by Dean Stark extraction with toluene, which showed very little imbibition.

Figures 4-5 show spontaneous imbibition data measured on plugs cleaned by the strong-solvent method that has previously been used to clean core plugs to a water-wet state (Table 1). These are compared to the wettability references discussed above. Those cut with oil-based mud imbibed very little brine, regardless of details such as cleaning temperature or composition of the oil used to measure imbibition. Only the aquifer core cut with water-based mud showed water-wet behavior. This shows that the rock is not

inherently mixed-wet or oil-wet, and that the imbibition results are neither sensitive to the type of oil used in the measurements, nor its pre-treatment. The core cut from the aquifer was used as a third reference for subsequent spontaneous imbibition results.

Development of 11-Step Method
Development of a successful cleaning method was an iterative process involving various core treatment methods and approximately 40 spontaneous imbibition tests. The initial approach was to use additional solvents in combination with the typical solvent sequence at 150°F. The following treatments were found to be ineffective in cleaning the cores to a water-wet state (Figure 6). In each case, they were added to the end of the strong solvent sequence shown in Table 1.

- methylene chloride
- acetone
- isopropanol (70%)
- slightly acidified brine (5.4 pH, 0.2 molar NH_4Cl), followed by n-propanol (This method was an attempt to put the fatty acid molecules in a non-ionized state using a mildly acidic solution, then dissolve them using a polar organic solvent.)
- 3-day soak with brine containing 3% hydrogen peroxide (This method was an attempt to chemically remove the fatty acids by reacting them with a strong oxidizing agent.)

Fatty acids react with bases to form salts that are usually soluble in water. Sodium hydroxide and other basic solvents have been used to remove contamination from polar crude oils on carbonates (Cuiec, 1975). Ammonium hydroxide has also been shown in past work to be effective at removing fatty acid contamination from core (Gant and Anderson, 1988). Therefore, alkaline solutions were examined for their effectiveness in returning the contaminated cores to a water wet state. Several iterations and solutions were examined, resulting in the following observations:

- Flushing cores with a KOH solution caused a slight permeability reduction, but this was less severe than flushing with reservoir brine containing various concentrations of NaOH (Figure 7).
- A plug that was re-used for a second cycle of alkaline flow-through cleaning (1 M KOH following 0.1 M NaOH and intermediate solvents) was more water-wet than plugs that had undergone only a single cycle (Figure 8).
- Cores cleaned with 2 cycles of 1 molar KOH solution were more water-wet than those cleaned with 2 cycles of 0.1 molar KOH solution (Figure 9).
- Synthetic Terra Nova brine formed a precipitate when contacted by high-concentration alkaline solutions. This was probably due to the formation of calcium and magnesium hydroxides, both of which are insoluble. This led to the use of an intermediate brine containing no calcium or magnesium.
- An attempt was made to simplify the core flushing procedure by using a solution of KOH dissolved in organic solvents (methanol and toluene), but this did not establish strongly water-wet conditions (Figure 10).

Successful Cleaning Method

After a number of iterations, an 11-step flow-through cleaning process was identified, which established a water-wet state while causing minimal damage to the permeability of the rock. This process is summarized in Table 3. The process combines the use of solvents (to remove bulk organic materials), an alkaline solution (to solubilize the fatty acids), and a neutral-pH brine (to establish pH conditions that allow adsorption of crude oil components during aging (Buckley, 1989)).

Figure 11 shows the results of spontaneous imbibition measurements conducted on three core samples subjected to the 11-step cleaning process. These are compared to the references discussed above. The behavior of the cleaned cores and the water-wet references was similar enough to justify adopting the 11-step method for cleaning the remainder of the SCAL plugs. Following cleaning and establishing connate water saturation, the plugs were aged at elevated temperature. Dead crude oil was metered into the core plugs or composite cores, and they were aged for at least 6 weeks, occasionally being flushed with fresh dead crude oil.

Steady-State Water-Oil Relative Permeability

One of the original goals of the Terra Nova SCAL program was to obtain water-oil relative permeability data. After development of the 11-step method, relative permeability was measured on a composite core made up of plugs that had been cut with an oil-based mud, cleaned, and aged to restore wettability. A similar measurement was carried out on core from the aquifer that had been cut with a water-based mud, cleaned with the solvent-only sequence shown in Table 1, and aged to establish a wettability state like that in the oil zone of the reservoir.

Properties of the composite cores are shown in Table 4, and results of these tests are compared in Figure 12. The excellent agreement indicates that the 11-step cleaning method brought the contaminated core to the same condition as aquifer core that had not been exposed to fatty acids. Both composites exhibited the mixed-wet behavior that is typical of most reservoir rock, including a final water relative permeability of approximately 0.5.

CONCLUSIONS

1. A special core cleaning method using KOH and solvents has been developed for removing contamination from oil-based mud containing fatty acid emulsifiers.
2. Core that was contaminated and cleaned showed similar behavior to core cut with water-based mud that had been cleaned only with solvents. The similar behavior was observed in (a) cleaned-state spontaneous imbibition tests, and (b) restored-state relative permeability tests.
3. For the rock used in this study, KOH was found to be less damaging to permeability than NaOH.
4. Two cycles of flushing with solvents and an alkaline solution were found to be more effective than a single cycle.

REFERENCES

Anderson, W.G., "Wettability Literature Survey - Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *J. of Petroleum Technology*, (Oct 1986), 1125-1144.

Ballard, T.J., and Dawe, R.A., "Wettability Alteration Induced by Oil-Based Drilling Fluid," SPE 17160 presented at the SPE Formation Damage Control Symposium, February 8-9, 1988, Bakersfield, CA.

Buckley, J.S., Takamura, K., and Morrow, N.R., "Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils," *SPE Reservoir Eng.*, (Aug 1989), 332-340.

Crago, A., "Differential Concentration of Non-Metallic Minerals," U. S. Patent 2,105,807, January 18, 1938.

Cuiec, L., "Evaluation of Reservoir Wettability and Its Effect on Oil Recovery", in *Interfacial Phenomena in Petroleum Recovery*, N.R Morrow, ed., Marcel Dekker, Inc., New York, p 319.

Cuiec, L.E., "Restoration of the Natural State of Core Samples," SPE 5634 presented at the 50th Annual Fall Meeting of the SPE, Sept. 28-Oct. 1, 1975, Dallas, TX.

Gant, P.L., and Anderson, W.G., "Core Cleaning for Restoration of Native Wettability," *SPE Formation Evaluation*, (Mar 1988) 131-138.

Jadhunandan, P.P. and Morrow, N.R., "Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems," *SPE Reservoir Eng.* (Feb 1995) 40-46.

Kovscek, A.R., Wong, H., and Radke, C.J., "A Pore-Level Scenario for the Development of Mixed Wettability in Oil Reservoirs," *AIChE Journal* (1993), **39**, 6, 1072-1085.

Menezes, J.L, Yan, J., and Sharma, M.M., "The Mechanism of Wettability Alteration Due to Surfactants in Oil-Based Muds," SPE 18460 presented at the SPE International Symposium on Oilfield Chemistry, February 9-10, 1989, Houston, TX.

Rezaei Gomari, K.A., Denoyel, R., and Hamouda, A.A., "Wettability of Calcite and Mica Modified by Different Long-chain Fatty Acids (C_{18} acids)," *Journal of Colloid and Interface Science* 297 (2006) 470-479.

Tong, Z. and Morrow, N.R., "Variations in Wetting Behavior of Mixed-Wet Cores Resulting from Probe Oil Solvency and Exposure to Synthetic Oil-Based Mud Emulsifiers," *Journal of Petroleum Science and Engineering* (2006) **52**, 149-160.

Thomas, D.C., Hsing, H., and Menzie, D.E., "Evaluation of Core Damage Caused by Oil-Based Drilling and Coring Fluids," SPE 13097 presented at the 59th Annual Technical Conference and Exhibition, September 15-19, 1984, Houston, TX.

Thomas, M.M, Clouse, J.A., and Longo, J.M., "Adsorption of Organic Compounds on Carbonate Minerals 3. Influence on Dissolution Rates," *Chem. Geol.* (1993), **109**, 227-237.

Wang, F.H.L., "Some Aspects of Wettability Alteration, Restoration, and Preservation," Proc. of the 3rd International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, September 21-23, 1994, Laramie, Wyoming.

Wendel, D.J., Anderson, W.G, and Meyers, J.D., "Restored-State Core Analysis for the Hutton Reservoir," *SPE Formation Evaluation*, (Dec 1987) 509-517.

Yan, J-N., Menezes, J.L, and Sharma, M.M, "Wettability Alteration Caused by Oil-Based Muds and Mud Components," *SPE Drilling & Completion* (Mar 1993) **8,** 1, 35-44.

Zhang, X., Morrow, N.R. and Ma, S., "Experimental Verification of a Modified Scaling Group for Spontaneous Imbibition," *SPE Reservoir Eng.* (Nov 1996) 280-285.

Zhang, Y., Bell, D.A., Chen, G., Morrow, N.R., and Buckley, J.S., "Cleaning Cores After Contamination with Synthetic Oil-Based Mud Components", Paper A-12 presented at 9th International Symposium on Evaluation of Wettability and Its Effect on Oil Recovery, September 18-19, 2006, Bergen, Norway.

Table 1: Typical Strong-Solvent Cleaning Process

Solvent	Temperature (^{o}F)	Completion Criteria
synthetic reservoir brine	72 - 150	2-5 pore volumes (PV)
toluene	72 - 150	5-10 PV and nearly colorless
87 wt.% chloroform/13 wt.% methanol	72 - 150	5-10 PV and nearly colorless
tetrahydrofuran	72 - 150	5-10 PV
methanol	72 - 150	3-5 PV
dry with nitrogen (low clay samples)	72 - 150	constant weight
OR synthetic reservoir brine (high-clay samples)	72 - 150	5-10 PV

Table 2: Properties of Crude Oil and Synthetic Formation Brine at Test Conditions

Fluid	Conditions	Density (g/ml)	Viscosity (cP)
synthetic Brine	72°F, atm pressure	1.0485	1.065
synthetic Brine	205°F, 4500 psig	1.022	0.407
dead Reservoir Crude Oil	150°F, atm pressure	0.834	4.55
live Crude Oil (reconstituted)	205°F, 4500 psig	**	0.91

Table 3: 11-step Cleaning Process to Establish a Water-wet Condition in Terra Nova Reservoir Core

	Solvent	Temperature (^{o}F)	Completion Criteria
1	methanol	150	50 cc
2	87 wt.% chloroform/13 wt.% methanol	150	100 cc
3	tetrahydrofuran	150	100 cc
4	methanol	150	50 cc
5	1 molar KOH solution	150	150 cc
6	methanol	150	50 cc
7	toluene	150	150 cc
8	methanol	150	50 cc
9	1 molar KOH solution	150	150 cc
10	calcium & magnesium-free synthetic reservoir brine	150	Until pH=7.0
11	methanol	150	100 cc
	oven dry at 150°F	150	constant weight

Table 4: Properties of Composite Cores Used in Relative Permeability Tests

	oil zone core	aquifer core
coring fluid	oil-based	water-based
cleaning method	11-step	solvents only (see Table 1)
effective permeability to oil at initial water saturation	641 mD	171 mD
irreducible water saturation (fraction)	0.108	0.151
porosity (fraction)	0.189	0.191
length	25.92 cm	17.90 cm
maximum relative permeability to water	0.459	0.643
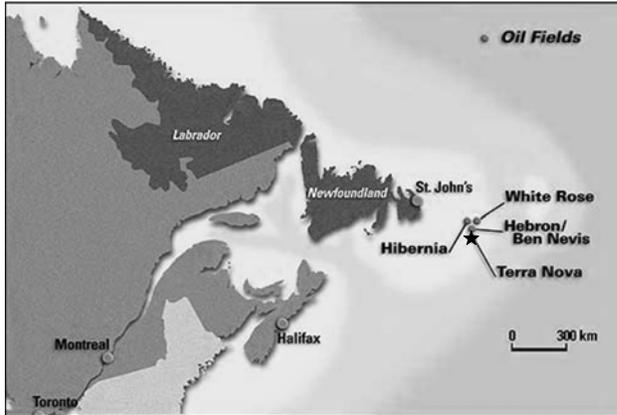
Figure 1. Terra Nova Field Location, Jeanne d'Arc Basin, offshore Newfoundland.
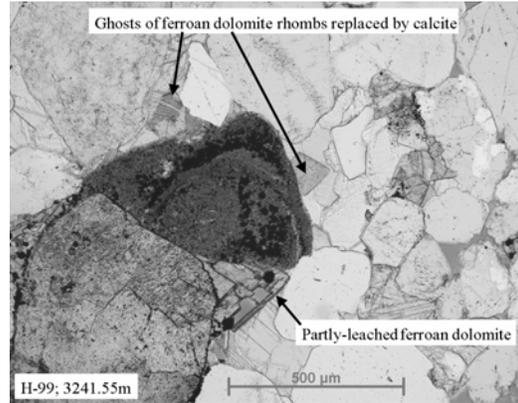
Figure 2. Thin section of Terra Nova core sample, showing carbonate cements**.**
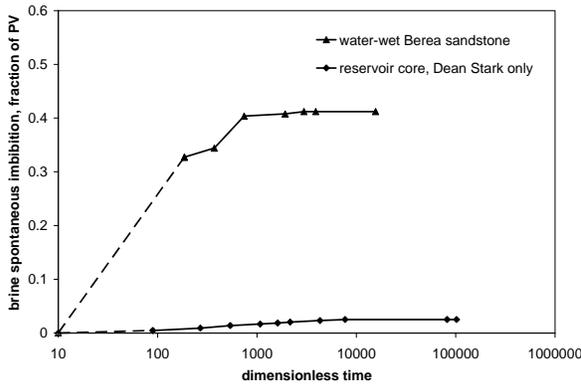
Figure 3. Wettability references for brine displacing tetradecane by spontaneous imbibition.
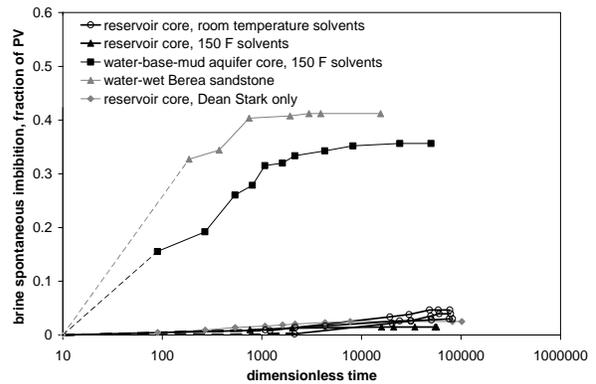
Figure 4. Brine displacing tetradecane by spontaneous imbibition into reservoir core cleaned with typical solvent sequence (Table 1).
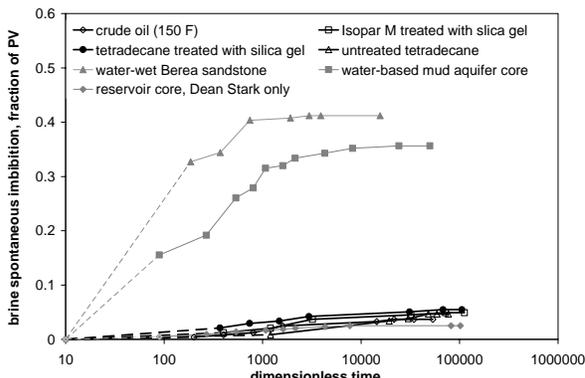
Figure 5. Brine displacing various hydrocarbons by spontaneous imbibition into reservoir core cleaned with typical solvent sequence.
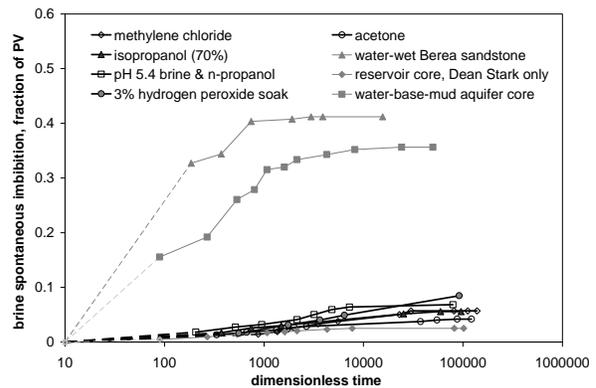
Figure 6. Brine displacing tetradecane by spontaneous imbibition into reservoir core cleaned by various chemical treatments after typical solvent sequence.
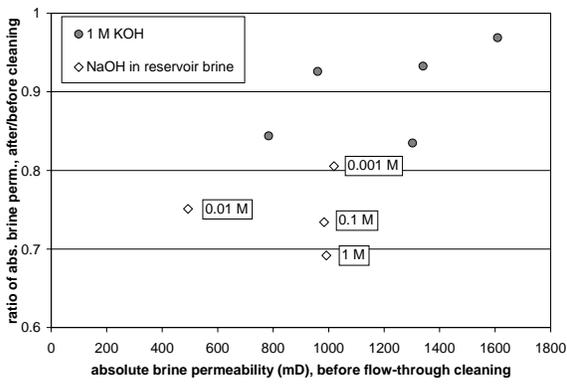
Figure 7. Comparison of absolute brine permeability after cleaning to absolute brine permeability before cleaning with KOH and various concentrations of NaOH.
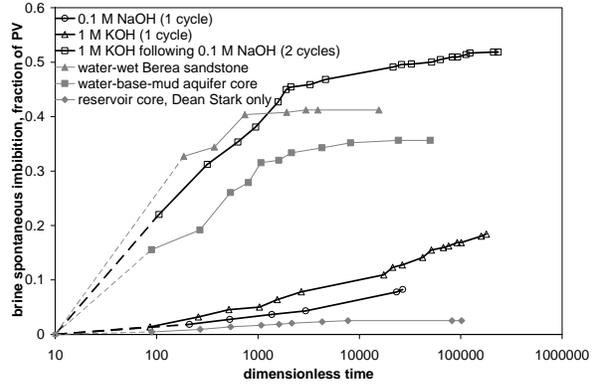
Figure 8. Brine displacing tetradecane by spontaneous imbibition into reservoir core cleaned with 1 cycle and 2 cycles of hydroxide.
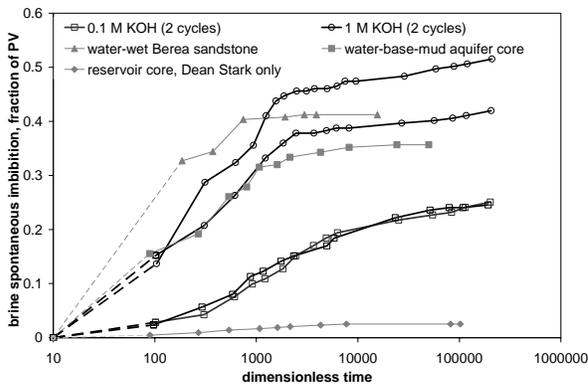
Figure 9. Brine displacing tetradecane by spontaneous imbibition into reservoir core cleaned with 2 cycles of 0.1 M and 1 M KOH.
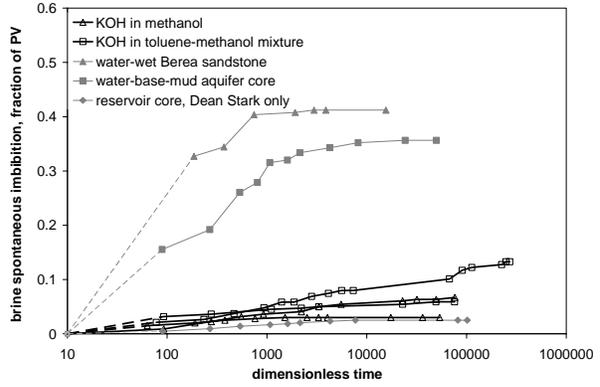
Figure 10. Brine displacing tetradecane by spontaneous imbibition into reservoir core cleaned with KOH in organic solvents.
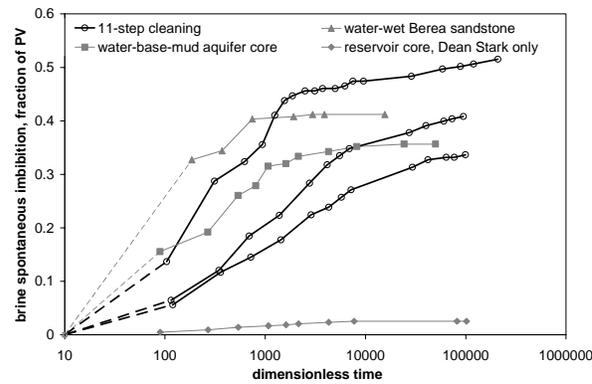
Figure 11. Brine displacing tetradecane by spontaneous imbibition into reservoir core cleaned with the 11-step cleaning method.
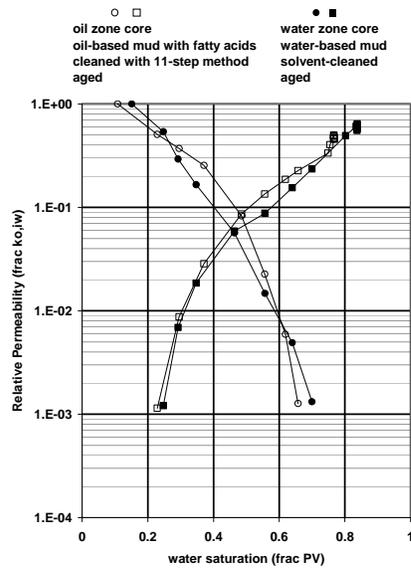
Figure 12: Water-oil relative permeability curves for contaminated core cleaned with the 11-step method, and uncontaminated core cut with water based mud.