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WETTABILITY EVALUATION DURING RESTORED STATE CORE ANALYSIS

by

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ABSTRACT

Wettability changes during stages of restored state core analysis were evaluated for a North Sea reservoir. The goal was to determine the proper technique for estimating the remaining oil saturation after waterflooding from core analysis.

The traditional methods for quantifying wettability, i.e., USBM and Amott indices and the Brownell-Katz correlation, were evaluated. It was found that the USBM and Amott procedures, when modified slightly, could be interpreted to give a good indication of wettability.

The traditional method of cleaning cores by Dean-Stark extraction with toluene followed by chloroform/methanol was found to be ineffective in making a core water-wet. To overcome this difficulty, we evaluated core cleaning procedures that employ a sequence of solvents. The remaining oil saturation increased from 9% with crude oil in the "as received" state to 28% with refined oil after the third cleaning.

Once the cores were made water-wet, aging the cores in a North Sea crude oil returned them to a mixed-wet state. However, the restored state cores were not as oil-wet as the "as received" state cores. Even after aging, there was a significant difference between the cores cleaned by Dean-Stark extraction and by a sequence of solvents. The mixed-wet condition with the North Sea crude oil is, therefore, expected to apply to the field: the crude oil base number, isoelectric point, effluent pH during core floods, and bottle wettability tests support this contention.

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Examination of the Brownell-Katz number correlation and the capillary pressure curves showed that much of the remaining oil saturation in a mixed-wet core during core analysis could be due to retention by a capillary end effect. This was supported by a CT scan of the core. In this mixed-wet reservoir, the remaining oil saturation is not equal to the residual oil saturation, but must be calculated using the appropriate relative permeability curve and the effect of buoyancy.

INTRODUCTION

There are two approaches for analyzing cores under the proper wettability conditions, "native state" and "restored state" analyses. (See Reference 1 for literature survey.) Native state analysis requires that the wettability state of the core be preserved at the in situ state. This requires that the core be protected from drilling fluid contamination, evaporation, oxidation, and freezing. If this could be accomplished successfully, it would avoid the effort of the restored state analysis. Since core preservation is often questionable and difficult to verify, however, restored state analysis is often used. Restored state analysis requires that the core be cleaned to the water-wet state that existed before oil accumulated in the formation. The core is then saturated with crude oil to a capillary pressure typical of the formation and the system allowed to equilibrate or "age" under conditions representative of those existing in the formation.

SYSTEM EVALUATED

Sandstone cores from a North Sea field, having brine permeabilities in the range 200–500 md and porosities of about 0.25, were used. The formation brine contained about 17,000 ppm TDS. The effluent brine pH from core floods ranged from 5.2–6.5 when the injected pH ranged from 6.5–8.2. Synthetic brine containing bicarbonate had a 5.1 pH when equilibrated with one atmosphere CO₂. The 35.4 API gravity crude oil has a base number of 1.40 mg KOH/g, an acid number of 0.08 mg KOH/g, and an isoelectric point at pH 5.9. In "bottle tests," the oil wets silica sand when the pH is 5.5 or less in 0.02 M NaCl. Thus, some degree of nonwater wetness is expected for this system.

SOLVENT EXTRACTION TO MAKE CORES WATER-WET

Cleaning sequence

The original plan of our study was to clean two cores using the traditional toluene Dean-Stark extraction, which removes water by boiling, and to clean another two cores using chloroform to remove the crude oil without first removing the water. The object was to compare the effect of the two methods on wettability. When neither method resulted in water-wet cores, additional steps were taken to achieve water wetness.

Cleaning Procedures

The cleaning steps are summarized in Table 1.

Table 1
INITIAL CLEANING SEQUENCE

Step	Cores	Solvent	Temperature	Time	Volume*
First	1,3	toluene	111°C	16 hours	–
	1,3	chl-meth	65°C	2 weeks	–
	2,4	chloroform	50°C	40 hours	2 liter
	2,4	chl-meth	50°C	40 hours	2 liter
Second	all	AMN		4 days	250 ml
		toluene		2.5 hours	150 ml
		chloroform		4 hours	250 ml
		chl-meth		4 hours	250 ml
Third	all	chl-meth		4 hours	250 ml
		methanol		4 days	250 ml/day
		brine	75°C	several hours	
Fourth	2,4	chloroform	50°C	4 hours	250 ml
		methanol	50°C	4 hours	250 ml
		methanol		2 days	250 ml/day

*Pore volume of each core is approximately 6.4 ml, and a pair were butted together for the flushing.

chl-meth = chloroform-methanol azeotrope

AMN = alphamethylnaphthalene

The Soltrol used to evaluate the wettability after the first cleaning was discolored on production from each core, indicating that the first cleaning was inadequate. Alphamethylnaphthalene (AMN) was chosen as the solvent for the next cleaning step based on a screening evaluation. The effluent was discolored when flow first started and for subsequent start-ups after overnight shut-in for the next three days. The AMN was flushed from the cores with toluene, followed by chloroform and then chloroform-methanol. The cores were then dried in an oven at 50°C for 16 hours.

The cores were cleaned for the third and fourth time because they failed to imbibe significant amounts of water spontaneously during the Amott test. A drop of water placed on the face of a dry core would form a drop for several minutes before imbibing into the core. Air-brine and oil-brine capillary pressure curves² compared closely with mercury-air capillary pressure curves, indicating water wetness in the interior of the core.

Effluent analysis

It was hypothesized that the lack of water imbibition was due to trace amounts of organic contaminants being concentrated at the external surfaces of the core by capillary wicking and evaporation of the solvent. The

core cleaning sequence using the "flush" method was repeated, and the effluent was analyzed by UV-visible spectrophotometry and gas chromatography. The reported concentration of "crude oil" is the concentration of crude oil that results in an equivalent amount of absorbance. The concentrations of the solutes in the effluent after the system had been shut in overnight are shown in Figure 1. With the exception of when the solvents were changed, the flowing concentrations were far less than the shut-in concentrations. The final methanol flush was visibly colored, but the equivalent crude oil concentration could not be determined because the spectra were so dissimilar. A final flush with tetrahydrofuran (THF) had 1341 ppm crude oil (equivalent absorbance) in the first pore volume. Crude oil components continue to be slowly extracted by THF.

The effluent analysis demonstrates that the solvents were extracting a significant amount of crude oil components and the prior solvents even when the flowing effluent looked clear. The difference between the flowing and the shut-in concentrations showed that contact time was more important than throughput. Oven drying the final solvent from the core will likely contaminate the faces of the core with crude oil components and AMN. The core should be dried by flowing humidified air through the core if it must be dried and subsequently used for spontaneous imbibition measurements.

Solvent screening and recommendation

The slowness of the above sequence of solvents in removing the crude oil and prior solvents motivated a search for more effective and universal solvents. A universal solvent should dissolve both wax and asphaltenes and have a small molar volume. It should be either a Lewis acid or a Lewis base³ such that it interacts more strongly with the crude oil components and/or mineral surfaces than it does with itself. It should not change the equilibrium pH of the core. Finally, it should be easily removed from the core.

A synopsis of the evaluation of several solvents is given in Table 2. The solvency was evaluated by observing the dissolution of a paraffin wax (Gulfwax) and an asphaltene (Peace River). Also listed are the solubility parameter (SP) of the solvent along with its dispersion (D), Lewis acid (A) and Lewis base (B) contributions,⁴ and molar volume. N-eicosane and anthracene are listed as models for wax and asphaltene, respectively, with known solubility parameters. While AMN is a good solvent for asphaltene because of the matched solubility parameter, it is a poor solvent for wax because of the dissimilar solubility parameter and large molar volume. Based on wax and asphaltene solvency, toluene, chloroform, and THF appeared to be good candidates. However, the former two solvents have already shown to be inadequate in cleaning cores to water wetness.

Table 2

SOLVENT SCREENING: SOLUBILITY PARAMETER, VOLUME, AND SOLVENCY⁴

Solvent	SP	D	A	B	Volume	Wax	Asphaltene
n-eicosane	16.3	16.6			359.8		
anthracene	20.3				138.9		
AMN	20.3	17.9			138.8	I	S
toluene	18.2	18.2	0.0	1.2	106.8	S	S
chloroform	19.0	16.6	13.3	1.0	80.7	S	VS
methanol	29.7	12.7	17.0	17.0	40.4	I	I
chl/meth						I	VS
THF	18.6	15.5	0.0	7.6	81.8	S	VS
DMSO	24.5	17.2	0.0	10.6	71.3	I	I
acetone	19.6	13.9	0.0	6.1	72.3	I	I
AMN	alphamethylnaphthalene						
chl/meth	87:13% wt (azeotropic mixture)						
THF	tetrahydrofuran						
DMSO	dimethylsulfoxide						
SP	solubility parameter, MPa ^{1/2}						
D	dispersion component, MPa ^{1/2}						
A	Lewis acid component, MPa ^{1/2}						
B	Lewis base component, MPa ^{1/2}						
I	10:90 vol. not dissolved						
S	10:90 vol. dissolved						
VS	10:90 dissolved in minutes						

A test was designed to evaluate if adsorbed solvent could change the wettability of a substrate. Water-wet glass slides (Fisher finest) were soaked in the solvents listed in Table 3, flushed with water, and soaked in water for 15 minutes, and the drainage of water was observed. THF made the glass nonwater-wet, but water wetness could be restored by overnight soaking in chloroform or acetone. Apparently, THF, which is a Lewis base, interacts with acidic sites on the glass but also interacts with chloroform, which is a Lewis acid.

Table 3

WETTING OF GLASS SLIDES BY WATER AFTER CONTACT WITH SOLVENT

First	Second	Observation
meth		F
chl		D
chl	meth	R
chl/meth		D
chl/meth	meth	R
AMN		F
AMN	meth	F
toluene		F
acetone		F
THF		D
THF	meth	D
THF*	meth (3 days)	F
THF*	acetone	F
THF*	chl	F
First	Soaked in first solvent 6 days	
*	Soaked in first solvent 40 days	
Second	Soaked in second solvent overnight	
F	Film drainage with interference fringes	
R	Rivulets	
D	Droplets	

All observations were after flushing and soaking in water for 15 minutes.

A recommended sequence of solvents is to flush initially with toluene or chloroform to remove the bulk of the oil without removing water. This is to be followed with THF to remove the remaining oil and most of the water, followed by chloroform-methanol to desorb THF, and finally methanol to remove the prior solvents, salt, and any remaining water. If the brine has very high salinity or if the core has dried, a methanol/water mixture may be needed prior to THF to remove the salt that may be shielding oil.

We have used THF to flush a core from another field that had been previously cleaned with alternating toluene and methanol Dean-Stark extractions. The first tenth of a pore volume had discoloration equivalent to 5200 ppm crude oil. Significant discoloration again occurred when the core was subsequently flushed with chloroform-methanol azeotrope.

Iron reduction

X-ray diffraction analysis showed most cored intervals contained pyrite. Stored core samples for this study had rusty spots, presumably as the result of oxidation of the pyrite in the wet environment of the stored core. A coating of iron oxides on sand grains can change the wettability as a result of changing the zeta potential of the sand grains and changing the density of the hydrogen-bonding, hydroxyl sites on the surfaces. At the present time, we do not know the effect of the iron oxides on wettability of this system. Another system became more water-wet as a result of a coating of iron hydroxide on quartz sand.

The restored state analysis with crude oil had the core restored to a reduced state, and efforts were made to maintain this state. Sodium dithionite solution at a concentration of 250 ppm active material or 500 ppm total was injected in synthetic brine to restore the core to a reduced state. Analysis of the effluent using a flow injection analyzer (FIA) is shown in Figure 2. The vertical dashed lines show when the system was shut in. Each flow period was at most one day. The iron and dithionite curves have the units of adsorbance. The redox potential units are mV relative to a Ag/AgCl electrode. The pH units are pH multiplied by 100. There were no iron data collected during the period between the second and third shut-in periods.

The peak iron concentration was about 40 ppm. The main portion of the iron was removed after 12 PV, but the trailing concentrations indicate that the system is not completely reduced. The dithionite concentration and redox potential stabilized during each flow period. The jump in iron concentration and redox potential and the drop in dithionite concentration after each shut-in period indicate that either the system is slow to equilibrate or that oxygen is entering the system during shut-in periods.

HOW IS WETTABILITY MEASURED?

The centrifuge: A tool for wettability evaluation

In this investigation, the automated centrifuge² was used to evaluate wettability and oil displacement: it is used to establish initial conditions and to displace to residual saturations. The capillary pressure and relative permeability curves determined from the centrifuge data are petrophysical parameters used for reservoir engineering calculations. Wettability parameters are determined from the capillary pressure curves.

USBM and Amott indices

The USBM^{5,6} and Amott^{6,7} indices are quantitative measures of wettability that are derived from the imbibition and secondary drainage capillary pressure curves. We measure a modified USBM index, which is the logarithm of the ratio of areas under the secondary drainage (oil saturation increasing) and imbibition (water saturation increasing) capillary pressure curves. (The original USBM method used the area under the capillary pressure versus average saturation curve. With curves of P_c versus saturation and average saturation available for the modified method, the areas can be easily determined by integration by parts.) The USBM index is positive with increasing magnitude as water wetting increases and is negative with increasing magnitude as oil wetting increases. Neutral wetting has an index value near zero. A system is considered strongly water-wetting or oil-wetting if the index is near +1.0 or -1.0, respectively.

The Amott index is the fraction of the total displaceable fluid that is produced by spontaneous imbibition. For a strongly water-wet system, this index is about 0.9–1.0 to displacement by water; for a strongly oil-wet system, this index is about 0.9–1.0 to displacement by oil.

The secondary drainage and imbibition results for Core 2 are shown in Figures 3 and 4; the capillary pressure is positive for drainage and negative for imbibition. The experiment started at connate water saturation with spontaneous and then forced (centrifugal) displacement with water. A spontaneous and then forced secondary drainage with oil followed. The experimentally measured saturations extrapolated to infinite time are shown as open symbols. The dashed curves passing through the data are average saturations calculated from capillary pressure model parameters that result in a best fit of the data. The solid curves are capillary pressure curves calculated using these parameters. The areas under the curves are hatched to the right under the secondary drainage curve and to the left under the imbibition curve. The other two curves, labeled "MERCURY" and "MIXED" (described in the next paragraph), are based on mercury-air data on an adjacent core sample.

The capillary pressure data in Figure 3 are for a case in which the core was in the "as received" wettability state and crude oil for the oil phase. (This may not be the "native state" as the wettability could have changed during the two-year period the core was stored.) The USBM index for this sample is -1.12 , a value that is considered oil-wet. Compared with the "MERCURY" curve, which has a zero irreducible saturation, the "OIL FLOOD" capillary pressure curve becomes vertical, indicating that the water is trapped as a discontinuous phase. The imbibition capillary pressure curve has a zero irreducible oil saturation. If the system is strongly oil-wet, then the oil-wet imbibition (waterflood) capillary pressure curve would be the negative of the MERCURY curve with oil saturation substituted for water saturation. Such a curve does not seem to describe the experimental results, however. By contrast, suppose that the smallest pores are water-wet and that all of the larger pores are oil-wet^{8,9}. Then, such a "MIXED WET" capillary pressure curve is a translation of the oil-wet curve by an amount equal to the connate water saturation (e.g., 25%). This curve has a zero oil saturation at a finite negative value of the capillary pressure, similar to the experimental result.

The Amott indices for the "as received" core are both small, indicating that it is neither strongly water-wet nor strongly oil-wet but that both phases are connected at their respective "residual" saturations.

Figure 4 shows the wettability measurements after the core had undergone three steps of cleaning. A refined oil (Soltrol 130) was used to evaluate the wettability of this "cleaned" core. The "OIL FLOOD" capillary pressure curve has the appearance of a water-wet curve. The imbibition capillary pressure has an irreducible oil saturation of 31% and the capillary pressure curve is vertical, indicating that the oil is trapped as a discontinuous phase. The 31% irreducible oil saturation is still low compared to the expected water-wet value of 37.5% from CCI. The USBM index is 1.00 indicating that the core is water-wet. However, the Amott index indicates that it is not completely water-wet, since only 54% of the oil production occurs by spontaneous water imbibition. The Amott index of 0 for spontaneous oil imbibition indicates that the oil was trapped as a discontinuous phase.

USBM Indices

The USBM indices are shown in Figure 5. The “as received” state cores have negative indices, indicating that they are more oil-wet than water-wet. After the third cleaning, the USBM indices for the cores are similar, but still less than the expected value (>1.0) for strongly water-wet conditions. The imbibition capillary pressure curves have a capillary entry pressure that appears to inhibit spontaneous imbibition of water. This may be due to contaminants on the external surfaces of the core, as mentioned earlier.

Amott Indices

The Amott index for spontaneous/total displacement by water is shown in Table 4. The original cores had little spontaneous water imbibition. After cleaning, there was less spontaneous water inhibition in all but Core 2. Core 2 had some spontaneous water imbibition after cleaning but less than that expected for strongly water-wet conditions. However, the lack of spontaneous water imbibition in three of the cores after cleaning was unexpected. It is this lack of spontaneous water imbibition, while the residual oil saturations and primary drainage capillary pressure curves indicated water-wet conditions, that made us suspect that the inflow faces may have been contaminated.

The Amott index for spontaneous/total displacement by oil is also shown in Table 4. Spontaneous oil imbibition occurs in all of the cores in the “as received” state, indicating that the oil is a connected phase at residual oil saturation. After cleaning, none of the cores had spontaneous oil imbibition.

Table 4

AMOTT INDICES TO EVALUATE CORE CLEANING (WATER FLOOD/OIL FLOOD)

Core No.	As Received	First	Second	Third
1	0.15/0.03	0.00/0.00	0.00/0.00	0.04/0.00
2	0.06/0.04	0.07/0.00	0.44/0.00	0.54/0.00
3	0.09/0.11	0.01/0.00	0.00/0.01	0.00/0.00
4	0.06/0.11	0.03/0.00	0.04/0.00	0.00/0.00

Capillary pressure curves

The average capillary pressure curve of the four cores at each stage of cleaning is shown in Figure 6. The drainage curve for the “as received” condition is vertical, indicating that water is trapped as a discontinuous phase. After cleaning, the drainage curves are more curved and go to lower water saturations. This is what one would expect for water-wet conditions.

The imbibition curve for the “as received” condition is curved and goes to zero oil saturation. This is an indication of film drainage. With each step of cleaning, the imbibition curves become more vertical and have a larger residual oil saturation. This is an indication that the oil is trapped as a discontinuous phase.

Residual oil saturation

Figure 7 shows the oil saturation after different stages of cleaning. These oil saturations are the final average oil saturations at the end of the single-speed experiment for the determination of the relative permeability (i.e., without extrapolation to infinite time or correction for end effect). The original cores were evaluated with stock tank crude oil and synthetic brine with the cores in the wetting state "as received." The cores had been stored for two years wrapped in plastic and aluminum foil. The cleaned cores were evaluated with Soltrol 130 and synthetic brine. The oil saturations increased from 9% for the original cores to 28% after the third cleaning. (The residual oil saturation from the capillary pressure data after the third cleaning averaged 32.6%; Figure 6.)

PRODUCING RESTORED STATE CORES: CORE CLEANING AND AGING WITH CRUDE OIL

Restored state core analysis requires cleaning cores to a water-wet state and then aging with crude oil at connate water saturation. The objectives of this part of the work were to compare results of (1) cores cleaned by the traditional toluene Dean-Stark extraction (DEAN-STARK) with a sequence of solvents (FLUSH), and (2) cores aged with crude oil with cores that have not been aged. The results reported in this section or in what follows are for four new plugs taken from the same piece of the North Sea core used in the work described above.

The results presented in this section will be reviewed in the context of the previous work. The cores "as received" were mixed-wet to oil-wet. The traditional Dean-Stark extraction followed by chloroform-methanol left the cores intermediate-wet. A sequence of solvents with adequate contact time was required to make the cores water-wet. Experiments with the North Sea crude oil show that it wets quartz at pH of 5.5 and below. Effluent of brine flushes through the core was pH 5.2-6.5. Thus, aging with this crude oil is expected to make the cores less water-wet, and this may reduce the contrast in wetting between the cores cleaned in two different ways.

Cleaning Procedures

Cores A and B were cleaned by Dean-Stark extraction with toluene for one day followed by chloroform-methanol extraction for 7 days. We found earlier that toluene Dean-Stark extraction will change an otherwise water-wet system to a less than water-wet state. We believe that this is because the toluene, which has a boiling point of 110.6°C, boils away the water before extracting the crude oil. In the absence of adsorbed water, crude oil components become strongly adsorbed on the mineral surfaces at sites that normally would be occupied by water. Subsequent contact of the surfaces with water may not displace the adsorbed crude oil components to restore the wettability.

Cores C and D were cleaned by the FLUSH method. The first stage was flushing with a sequence of (1) alphas-methylnaphthalene, (2) toluene, and (3) chloroform. This stage extracts most of the crude oil

without removing much of the water. The next stage was (4) chloroform-methanol and (5) methanol. This stage extracts the water and most of the crude oil that becomes exposed to the solvent as the water is being removed. The final stage of extraction is designed to remove the adsorbed crude oil components by first using a good solvent for asphaltenes followed by a sequence of solvents to extract the preceding solvents. These solvents are (6) alphas-methylnaphthalene, (7) toluene, (8) chloroform-methanol, and (9) methanol. The final solvent, methanol, is displaced by flowing nitrogen through the core. We previously discovered that oven drying deposited nonvolatile components on faces of the core. Any remaining adsorbed methanol is expected to be desorbed by water.

Since trace amounts of ferric ions are known to change the wettability of quartz, it was decided to restore the cores cleaned by the FLUSH method to a reduced state; we described earlier the procedure and results of restoring the cores to a reduced state.

Aging

The “before aging” capillary pressure curves were measured immediately after the cores were cleaned by the FLUSH method. Then, the cores at connate water saturation were sealed in a container of crude oil and aged in an oven at 150°F for 28 days. The FLUSH cleaned cores were treated with care in a nitrogen-filled glove box to avoid introduction of oxygen. Also, the brine for the imbibition experiments contained sodium dithionite.

RESULTS ON “RESTORED STATE” CORES

Capillary Pressure

The capillary pressures were measured in the sequence (1) imbibition and (2) secondary drainage. The capillary pressures were interpreted from the data by extrapolating the production to infinite time and fitting the data with a Thomeer model.¹⁰

USBM and Amott Indices

The USBM index for the cores before and after aging is shown in Figure 8. The DEAN-STARK method of cleaning made the cores less oil-wet than in the “as received” condition. The FLUSH method resulted in a neutral-wet condition. This is in contrast to the preferentially water-wet state when the FLUSH method was evaluated using refined oil. After aging for one month, cores cleaned by both methods became more oil-wet, but the DEAN-STARK cores were still more oil-wet than the FLUSH cores.

The Amott indices were equal to zero for all of the cores. Some spontaneous production could have occurred but not been observed because of retention on the surfaces of the core holder.

Residual Oil Saturation

Oil saturations at a capillary pressure of -11 psi are shown in Figure 9. These residual oil saturations are lower than the final oil saturation at the end of a single-speed experiment, reported earlier. The earlier estimates include some mobile oil saturation if some production was occurring at the end of an experiment and include the oil saturation held up by the capillary end effect if the capillary pressure curve was not vertical. Since the saturation held in the capillary end effect is dependent on the speed of the experiment, the final oil saturation is influenced by the speed and the duration of the experiment.

The oil saturations at $P_c = -15$ psi for the cores in the "as received" condition were zero, and the average value of the cores cleaned to a water-wet state and measured with a refined oil was 0.32.

These results show that aging with this crude oil significantly reduces the residual oil saturation. The DEAN-STARK cleaning method results in a lower residual oil saturation compared to the FLUSH method. We showed earlier that this is because the DEAN-STARK method does not make cores water-wet.

Connate Water Saturation

Water saturations at a capillary pressure of 6.8 psi are shown on Figure 10. The water saturation is higher for the cores cleaned by the Dean-Stark method. It is speculated that some water is trapped as a discontinuous phase as a result of the Dean-Stark extraction boiling off the water from the smaller pores and surface roughness and allowing these surfaces to be contaminated with crude oil components.

Relative Permeability

Relative permeabilities were measured with single-speed imbibition and secondary drainage experiments. The curves were interpreted using a finite mobility ratio, zero capillary pressure model (D. J. O'Meara, private communication). A speed less than the maximum speed of the centrifuge was used to collect sufficient data during the early times to get a good estimate of the end-point relative permeabilities. Thus, a significant correction for the capillary holdup is required in some cases. A method for taking this into account is being developed. Thus, the present relative permeability results are preliminary and should only be used for comparative purposes.

The absolute permeabilities for the four cores were measured from the end-point permeability of an air/oil drainage experiment using an 80 cp refined oil. The relative permeability curves are shown in Figure 11. The curves for the cores cleaned by the same method nearly overlay each other. The dashed part of the curve is the shock portion of the curve interpolated between the end point and breakthrough. The Dean-Stark cleaned cores have lower residual oil saturation and higher irreducible water saturation, indicating that they are less water-wet.

LABORATORY REMAINING OIL SATURATION

A distinction must be made between the residual oil saturation in laboratory experiments and the remaining oil saturation in the reservoir. If the system is strongly water-wetting, the residual oil saturation is unambiguous. In the case of mixed wetting, a reported residual oil saturation could be (1) the immobile oil saturation evaluated at zero relative permeability in an experiment with a large capillary pressure and production extrapolated to infinite time, (2) the oil saturation evaluated at a finite, negative capillary pressure, (3) the final average saturation in a core at some finite capillary pressure, or (4) the final average saturation in a flow experiment at some flow rate and after a finite throughput.

Saturation distribution in a centrifuge displacement

Graphs of oil saturation versus capillary number are used to determine the relation between residual oil saturation and interfacial tension, flow rate, buoyancy, and rock pore structure.¹¹ These relationships are usually measured with flow experiments and assume that the saturation is uniform along the core. An implicit assumption is that the oil is retained in the core as a trapped, discontinuous phase. King et al.¹² recognized that at low Bond numbers (ratio of buoyancy to capillary forces), the oil could be retained as a continuous phase in the form of a capillary end effect, and at high Bond numbers, the oil could be retained as a discontinuous phase. Morrow and Songkran¹³ determined the relation between capillary number (ratio of viscous to capillary forces) and Bond number that would correlate the trapping of a nonwetting phase. If the Bond number is defined with respect to the permeability rather than the bead radius, only a scale factor of 0.45 is required for the Bond number to have the same effect as the capillary number.

The effects of flow rate and centrifuge speed on the oil saturation in a mixed-wet system can be illustrated with wetting phase saturation profiles, as in Figure 12. In this illustration, the wetting phase is displaced by buoyancy forces in the case of a centrifuge experiment and by the pressure gradient of the injected phase in case of a flow experiment. In the case of a flow experiment, the saturation profiles will be only qualitatively similar, since the potential gradient is inversely proportional to the relative permeability of the invading phase. The wetting phase is retained at the outflow end by the condition of zero capillary pressure. At zero speed, the saturation has a uniform value equal to one minus the residual nonwetting phase saturation. At a low speed, the invading phase has invaded only a portion of the core, and there is a significant change in saturation across the core. The average saturation for the profile is shown by the solid symbol. This average saturation is directly measured in either the centrifuge or the flow experiment. As the speed increases, the invading phase invades a larger fraction of the core, and the profile approaches the irreducible saturation shown as the vertical dotted line. This irreducible or residual saturation, which is the discontinuous ("wetting" phase) saturation, could be independent of the centrifuge speed up to some critical value above which it will decrease. The concept illustrated here is that, in a mixed-wet system, the oil will be produced at low Bond numbers or capillary numbers as a continuous phase and at high Bond numbers or capillary

numbers by mobilization of a discontinuous phase. King et al.¹² reported that the transition to discontinuous flow occurs at a Bond number of about 10^{-5} . They could overlay the curves of residual oil saturation versus capillary number with the curves of residual oil saturation versus Bond number for Berea cores if the Bond number is adjusted by a factor of 0.5. However, for Prudhoe Bay cores, a factor of 200 was required to overlay the curves. A possible cause for this discrepancy is that they assumed there would be no end effect once discontinuous production sets in and, thus, used the saturation at the inflow end rather than the average saturation to compare with the flow experiments. The Prudhoe Bay cores could be mixed-wet and have a capillary end effect. There is no reason for the end effect to disappear entirely, and the average saturation could have been significantly larger than the inflow end saturation.

Brownell-Katz number

A correlation of the remaining oil saturation in a core with the Brownell-Katz number (N_{BK}) has been used to examine the effect of wettability on the residual oil saturation in a manner analogous to the examination of the effect of interfacial tension on residual oil saturation by correlating with the capillary number. However, we show here that the change of the remaining oil saturation with the N_{BK} in a mixed-wet system may not be due to a change in the residual oil saturation but rather to a change in the amount of oil held up by the capillary end-effect.

The equivalence between the capillary number and the Bond number is derived with the assumption that both phases are continuous. The capillary number, defined by Brownell and Katz,¹⁴ is as follows:

$$N_{BK} = k \nabla \Phi / \sigma = u \mu / k_{rw} \sigma . \quad (1)$$

The N_{BK} in terms of the capillary pressure is

$$N_{BK} = k P_c / \sigma L . \quad (2)$$

Thus, in a centrifuge experiment, N_{BK} is proportional to the capillary pressure.

Average oil saturations in the cores with "as received" wetting state are shown in Figure 13. These cores had slow production up to the 1000 minutes used for each centrifuge speed step, and the productions were extrapolated to infinite time. The extrapolated results are shown as the dashed curves. This slow production by "film drainage"⁹ indicates that the oil is being produced as a continuous phase. The average saturation is a continuously decreasing function of the N_{BK} . From capillary number correlations for the mobilization of a trapped nonwetting phase, a discontinuous oil saturation is expected to decrease only at a N_{BK} above

10^{-5} – 10^{-4} . Therefore, the oil produced in these experiments must be from a continuous phase that continues to produce to a low saturation by “film drainage.”

To interpret the relation between the oil saturation versus N_{BK} and wettability, calculated curves of average saturation versus N_{BK} number are shown for the oil-wet and mixed-wet capillary pressure curves previously discussed with Figure 3. These two calculated curves had initial oil saturations of 1.0 and 0.75, respectively. The experimental data have initial oil saturations ranging from 0.61 to 0.64 because of the trapped water discussed with Figure 3. The small amount of spontaneous water imbibition (Amott number 0.06 to 0.15), and the start of production at small N_{BK} numbers, indicate that the cores have some water-wet or intermediate-wet characteristics. The “OIL-WET” calculated curve has the same qualitative trend of decreasing average saturation, but the level of saturation is too high. The “MIXED WET” curve was calculated with a connate water saturation of 0.25 to match the experimental data. As mentioned earlier, the mixed-wet model assumes that oil wets all pores larger than the smallest pores, which contain the connate water. Since the oil wets these larger pores, it is a continuous phase that can flow by film drainage on the walls of the larger pores. When the (negative) capillary pressure increases to where the oil is displaced from the smallest pores that it originally occupied, the oil saturation is zero. The calculated average saturation as a function of the N_{BK} only approaches, but does not reach, zero, because there is always some oil saturation due to the end effect. The agreement of the mixed-wet model with the experimental data as well as the continuing production at 1000 minutes indicates that the oil is producing as a continuous phase, presumably by the film drainage mechanism, and that the oil retained in the core is due only to a capillary end effect and inadequate time for equilibration.

The average oil saturation in the cores as a function of N_{BK} after the third solvent extraction of the cores and using Soltrol as the oil is shown in Figure 14. The small amount of water imbibition (Amott index 0.0 to 0.54) indicates that the cores are not completely water-wet. The reduction in oil saturation below a N_{BK} of 10^{-6} suggests that some of the oil in this regime is produced as a continuous phase and is retained as a capillary end effect. The lack of continued production at 1000 minutes in some of the cores suggests that the oil is discontinuous. The plateau in the saturation at N_{BK} above 10^{-6} indicates that, in this regime, the oil is trapped as a discontinuous phase. The plateau values of the average saturations (which average 0.326) is a “residual oil saturation” for the core at this state of wetting. An adjacent core had a toluene-air countercurrent imbibition residual saturation of 0.375.

The residual oil saturation as a function of the N_{BK} calculated from the theory of Stegemeier¹¹ assuming water-wet conditions is also shown in Figure 14. The calculations were based on mercury-air capillary pressure data, toluene-air countercurrent imbibition data, $\psi = 0.8$, and $f = 10$. It shows that the water-wet residual saturation does not make a significant change until the N_{BK} exceeds 10^{-4} . All of the experiments in this report were at N_{BK} less than this value. Thus, the observed changes in the remaining oil saturation with N_{BK} should not have been due to displacement of a disconnected, nonwetting phase.

Measured saturation distribution

The distribution of remaining oil saturation in cores as a function of wettability was observed by employing CT scan technology.¹⁵ The water-wet case was the cleaned Core 2 with 75% hexadecane and 25% iodoheptadecane. The mixed-wet case was Core A (Dean-Stark cleaned), aged 92 days at connate water saturation with 75% crude oil and 25% iodoheptadecane. The centrifuge time at each speed was 1000 minutes. The cores were chilled to 1°C to solidify the oil to prevent fluid redistribution while the cores were scanned. The cores were scanned in the longitudinal direction in aluminum core holders.

The oil saturation distribution during the waterflood with the refined oil in the cleaned Core 2, Figure 15, shows little change from capillary pressures of -1.03 to -10.76 psi. A capillary end effect is just barely evident at the lowest capillary pressure. In contrast, the oil saturation distribution for the restored state, mixed-wet Core A, Figure 16, shows significant saturation change with increase in (negative) capillary pressure, and a significant capillary end effect is evident at all except the highest capillary pressure. The saturation distribution has the appearance of the mirror image of the primary drainage saturation distribution for Core 2. The presence of a finite capillary entry pressure (for waterflooding) is evident from the absence of any change in saturation for the two lowest capillary pressures.

These results are in contrast with the observations of Heaviside et al.¹⁶ for intermediate wettability cores and of Mohanty and Miller¹⁷ for mixed-wet cores. The end effects observed here are in accord with that observed by Hinkley and Davis¹⁸ for oil-wet butted core sections. Apparently, the system must be nonwater-wet enough and have low enough capillary pressure for the end effect to be observed.

The analysis for the remaining oil saturation as a function of the N_{Bg} assumed that the oil was a continuous phase. This assumption results in a remaining oil saturation distribution that is a function of the negative imbibition capillary pressure curve. If the oil phase remains continuous to low oil saturations, the oil relative permeability will be small but nonzero to low oil saturations, i.e., film drainage will be observed. On the other hand, if the oil is discontinuous, then one should not expect a capillary end effect, changing saturation with imbibition capillary pressure, or film drainage.

RESERVOIR REMAINING OIL SATURATION

In the case of mixed wettability where the oil flows at low saturations by film drainage, the remaining oil saturation in the swept zone of a reservoir must be calculated from the relative permeability curve and the reservoir parameters. A reservoir will have at most a few pore volumes of throughput but the buoyancy forces will act continuously on the oil after the flood front passes. The remaining oil saturation will then be a function of vertical position and time since the passage of the flood front. The remaining oil saturation distribution shown in Figure 17 was calculated by the method explained by Richardson et al.¹⁹ The oil relative permeability curve for the "as received" case shown here had a zero residual oil saturation and a

Corey exponent of 7.4. This value of the Corey exponent is equivalent to a Salathiel drainage exponent of -0.16 , similar to the value of -0.18 reported for the East Texas Field.⁹

CONCLUSIONS

How is Wettability Measured?

1. The USBM and Amott indices measured by the automated centrifuge are a good measure of wettability.

2. As a system becomes less water-wet, the discontinuous, trapped water saturation increases, and the drainage capillary pressure curve crosses the water-wet curve and becomes vertical at a water saturation higher than what would be expected for a water-wet capillary pressure curve. The area under the imbibition capillary pressure curve increases, and the irreducible or residual oil saturation decreases and can approach zero.

3. In a mixed-wet system, some of the oil is retained in the core as a capillary end effect: the oil saturation diminishes with increase in centrifuge speed or flow rate.

4. In "as received" cores using crude oil, the oil appeared to be retained entirely as an end effect that could be represented by a mixed-wet capillary pressure model.

5. After the cores had been cleaned with solvents, little of the oil appeared to be retained as an end effect and most was trapped as a discontinuous phase.

Solvent Extraction to Make Cores Water-Wet

6. The standard Dean-Stark extraction with toluene followed by chloroform-methanol did not achieve a water-wet condition for a core that initially was not water-wet.

7. The residual (remaining) oil saturation increased from 9% with crude oil in "as received" cores to 28% with a refined oil after the third cleaning of the core. The latter residual oil saturation is still less than the CCI value of 37.5%.

8. The USBM index increased from negative values with crude oil in the cores in the "as received" state to positive values with refined oil after the third cleaning. The magnitude of the latter values is less than the expected value for strongly water-wet conditions.

9. The Amott index for spontaneous/total displacement by water showed (with an exception) that cores fail to imbibe water spontaneously, even after the third cleaning. The Amott index of spontaneous/total displacement by oil is equal to zero after the third cleaning.

10. The oil-water and air-water primary drainage capillary pressure curves of cleaned cores agree with the mercury-air curve of an adjacent core.

11. The indications are that the interior of cleaned cores is water-wet, but the exterior surfaces are not water-wet. This may be due to wicking of contaminants to the external surfaces where solvents evaporate.

12. The contact time of the solvents with the core is as important as the volume throughput.

Producing Restored State Cores: Core Cleaning and Aging with Crude Oil

13. Core cleaning methods affect the restored state capillary pressures, relative permeabilities, and residual saturations. The traditional method of Dean-Stark extraction with toluene followed by chloroform-methanol did not adequately clean the cores, and the restored state cores were more oil-wetting than were more thoroughly cleaned cores; the cleaning methods made a difference of about 0.04 in the residual oil saturation after aging for one month with a North Sea crude oil.

14. Aging for one month with a North Sea crude oil made the cores more oil-wet. The residual oil saturation reduced by about 0.13 as a result of the aging.

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NOMENCLATURE

f	multipore oil filament length to radius ratio
g	gravitational acceleration, m/s
k	permeability, m ²
k_{ro}^o	end-point oil relative permeability
k_{rw}	water relative permeability
L	core length, m
N_{BK}	Brownell-Katz number
n	Corey exponent
P_c	capillary pressure, Pa
$\Delta\rho$	density difference, kg/m ³
S	reduced saturation
S_{oi}	initial oil saturation
S_{or}	residual oil saturation
t	time, s
u	flux, m/s
z	distance, m

Greek letters

μ	viscosity, Pa · s
Φ	flow potential, Pa
ϕ	porosity
σ	interfacial tension, N/m
ψ	geometrical factor for curvature

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SOLVENT FLUSHING OF CORES SHUT-IN CONCENTRATIONS

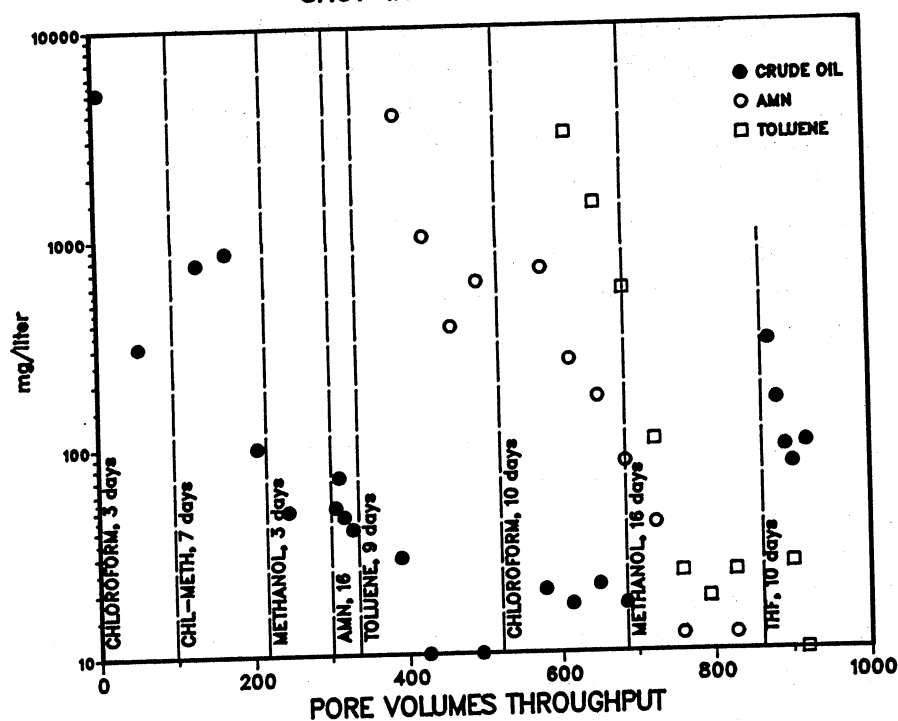


Fig. 1 - Shut-in solute concentrations during solvent flushing of cores.

RESTORATION TO REDUCING CONDITIONS

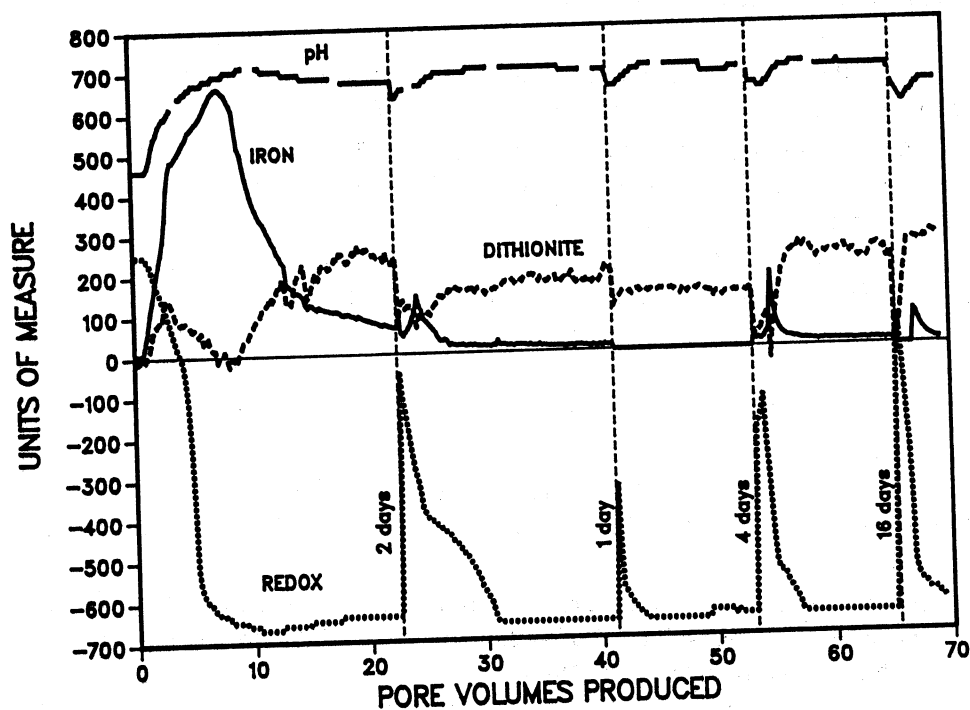


Fig. 2 - Effluent concentrations during the restoration of cores to reducing conditions.

EVALUATION OF CORE CLEANING USBM INDEX

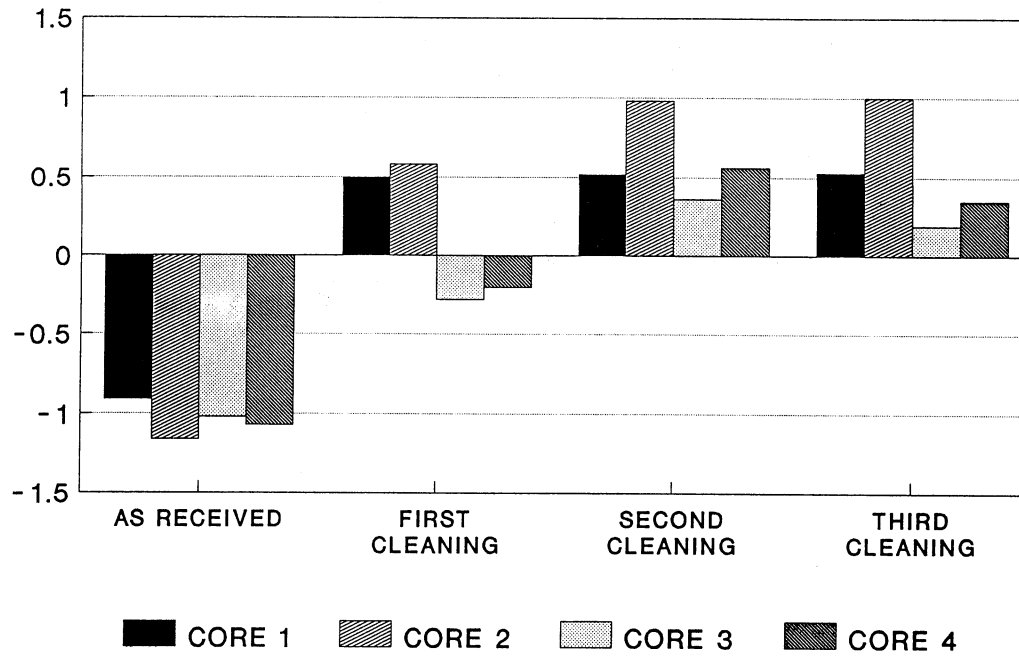


Fig. 5 – USBM index for evaluation of core cleaning.

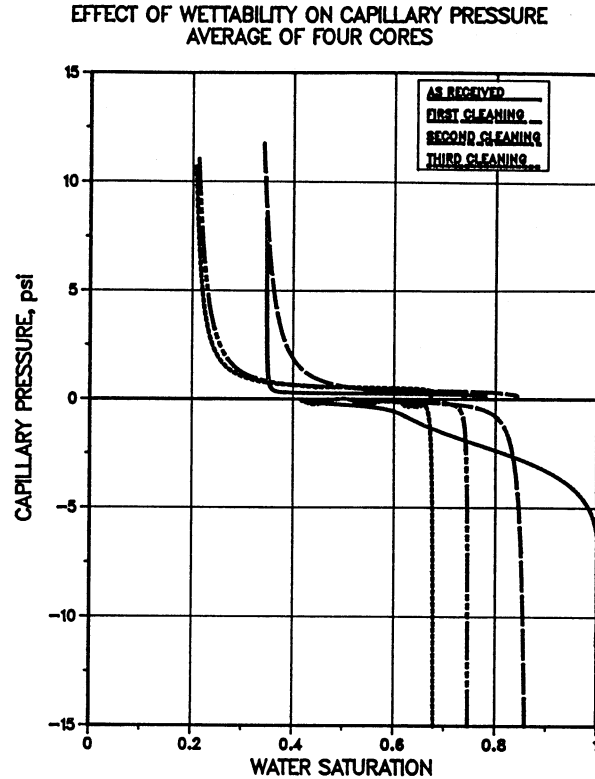


Fig. 6 – Imbibition and secondary drainage capillary pressure curves for evaluation of core cleaning; average of four cores.

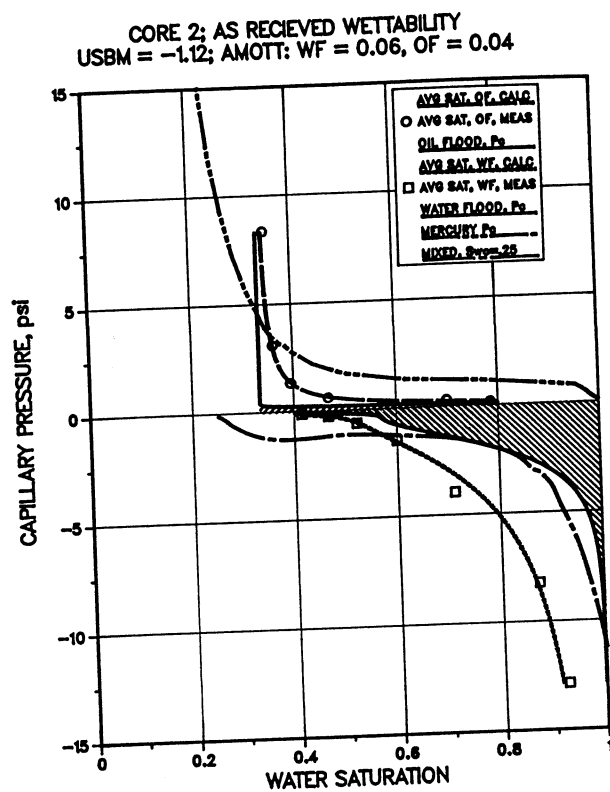


Fig. 3 – Imbibition and secondary drainage capillary pressure curves with crude oil in the “AS RECEIVED” cores.

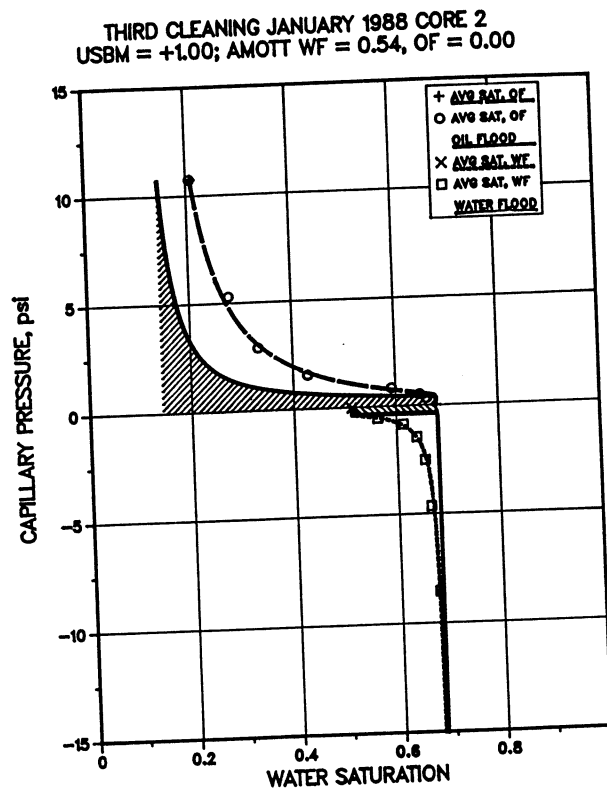


Fig. 4 – Imbibition and secondary drainage capillary pressure curves with refined oil after third cleaning of core.

RESTORED STATE RESIDUAL OIL SATURATION EFFECT OF CORE CLEANING AND AGING

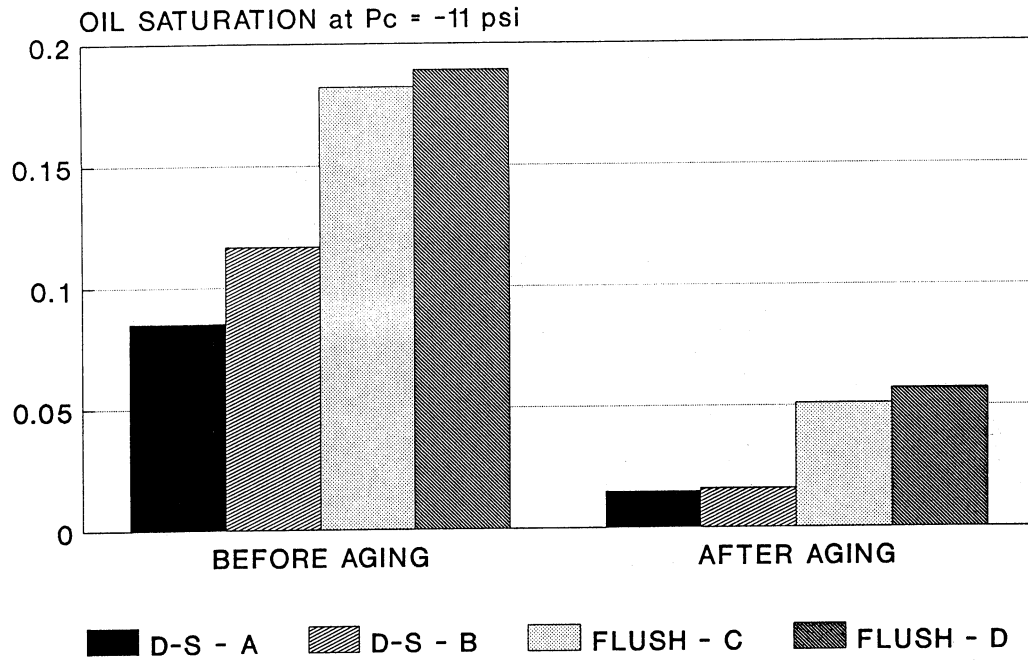


Fig. 9 – Remaining oil saturation for restored state analysis; effects of cleaning methods and aging.

RESTORED STATE CONNATE WATER SATURATION EFFECT OF CORE CLEANING AND AGING

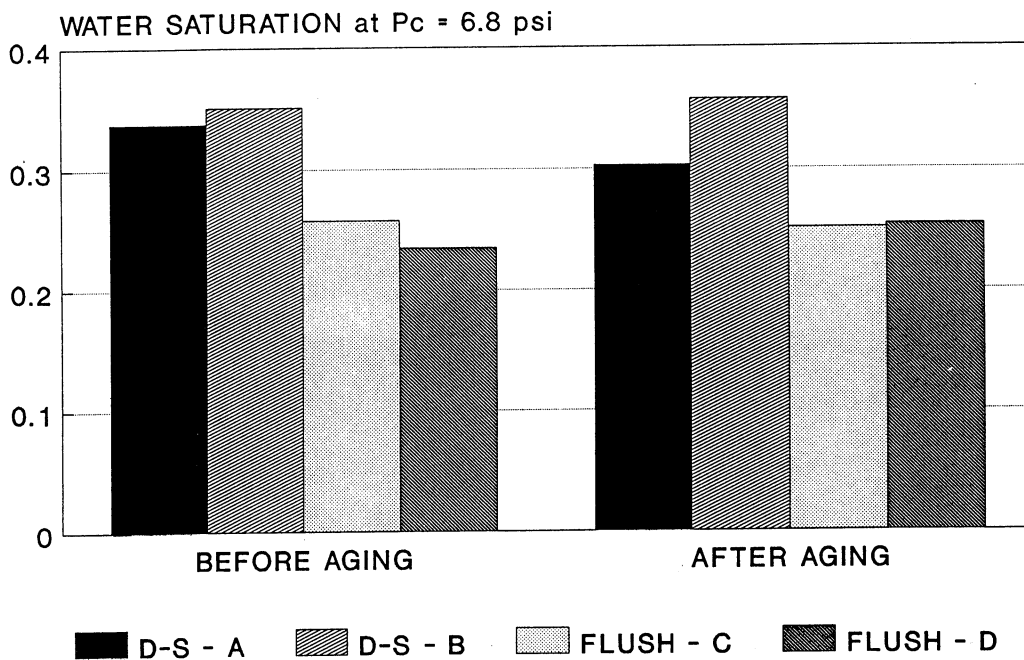


Fig. 10 – Connate water saturation for restored state analysis; effects of core cleaning and aging.

EVALUATION OF CORE CLEANING FINAL SATURATION AFTER SINGLE SPEED

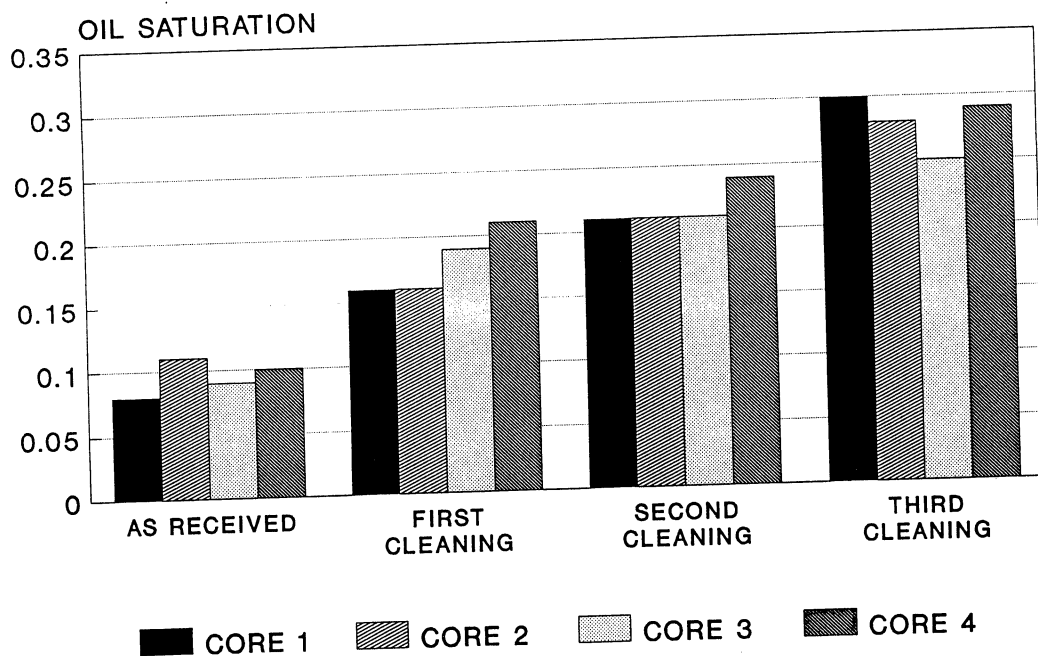


Fig. 7 - Remaining oil saturation in cores for evaluation of core cleaning.

RESTORED STATE USBM INDEX EFFECT OF CORE CLEANING AND AGING

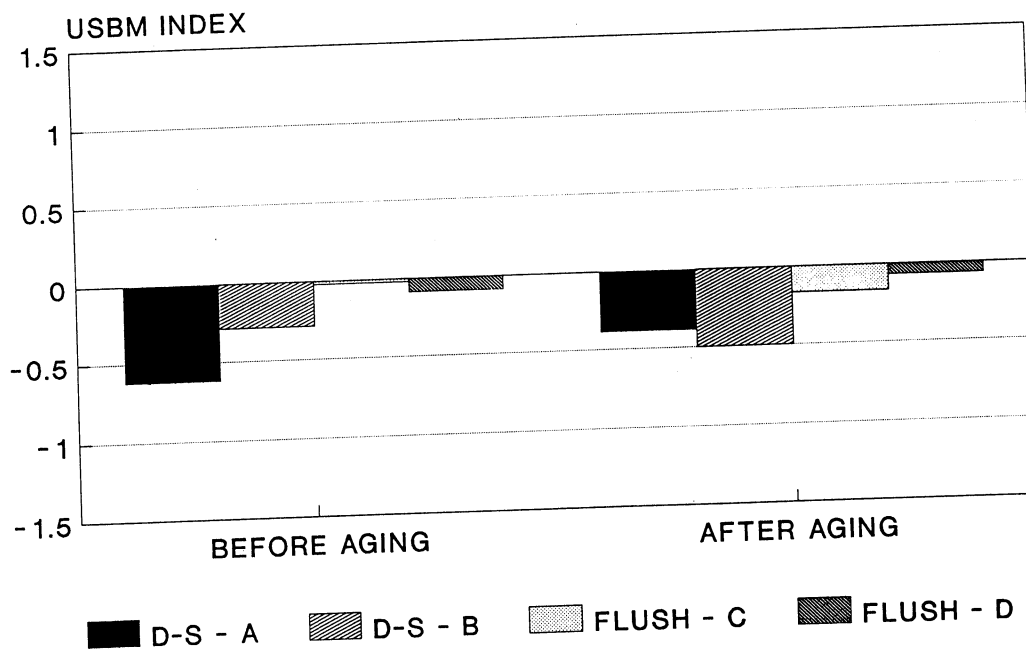


Fig. 8 - USBM index for restored state analysis; effects of cleaning methods and aging.

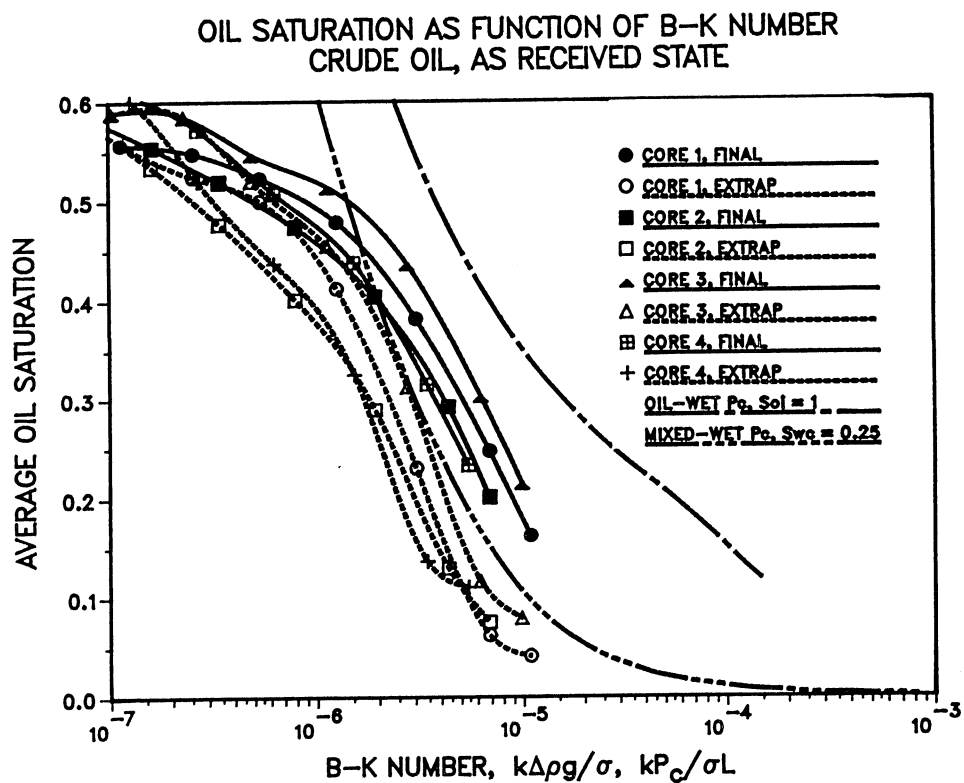


Fig. 13 - Remaining oil saturation in core as function of Brownell-Katz number, crude oil in "AS RECEIVED" state cores. Calculated curves are for oil-wet and mixed-wet models, using measured air-mercury capillary pressure curves.

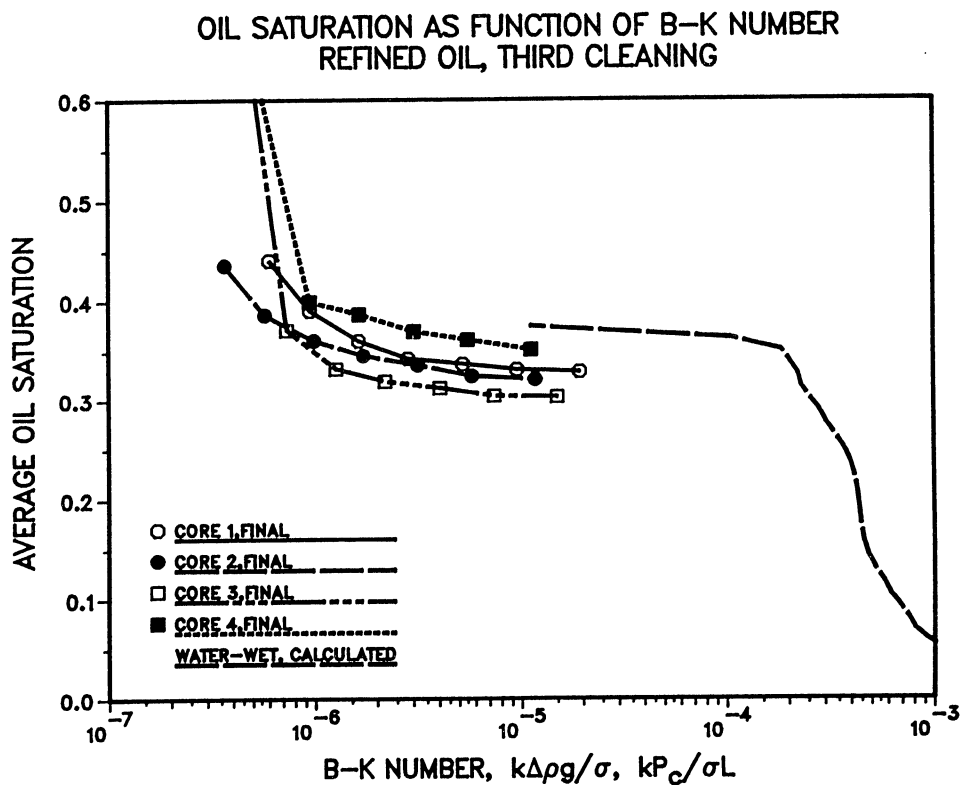


Fig. 14 - Remaining oil saturation in core as function of Brownell-Katz number, refined oil in cores after third cleaning. Calculated water-wet curve is from theory of Stegemeier¹¹ using measured initial-residual and air-mercury capillary pressure curves.

THE EFFECT OF CLEANING METHOD ON RELATIVE PERMEABILITY AGED CORES

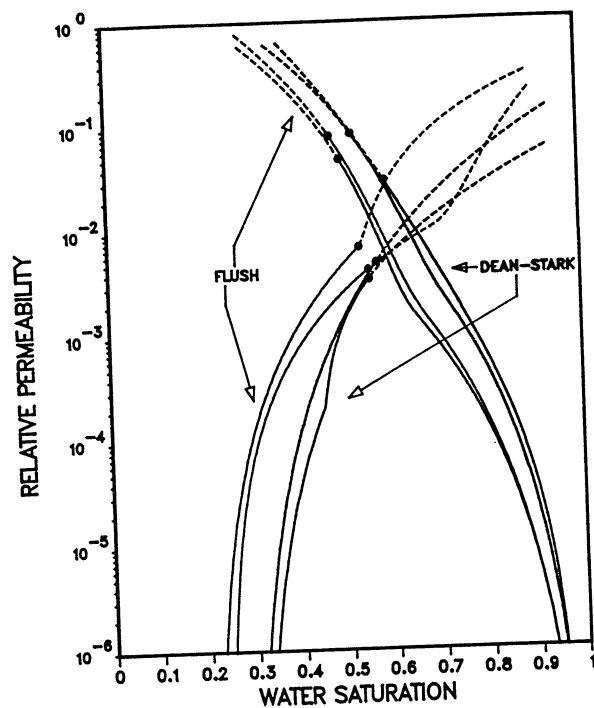


Fig. 11 – Relative permeability curves for restored state analysis; effects of core cleaning and aging.

EQUILIBRIUM WETTING FLUID SATURATION PROFILE IN CORE WITH CENTRIFUGE SPEED

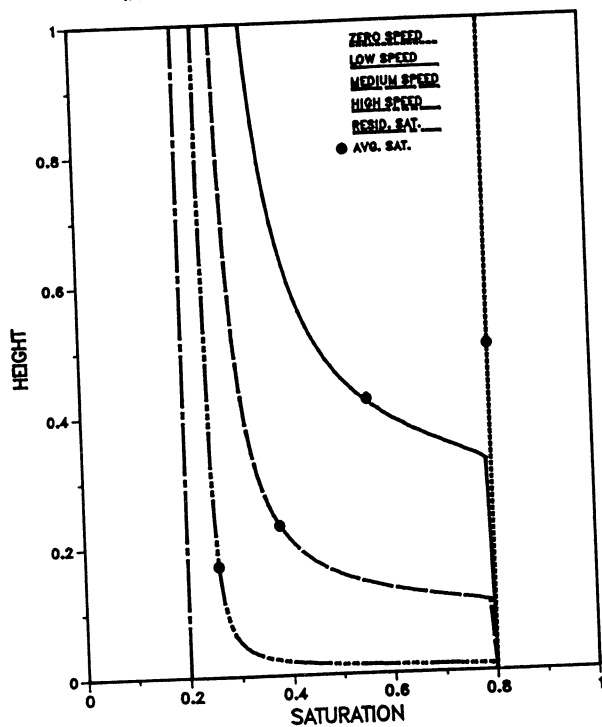


Fig. 12 – Saturation distribution of wetting fluid with increase of centrifuge speed, schematic. Dot is average saturation in core.

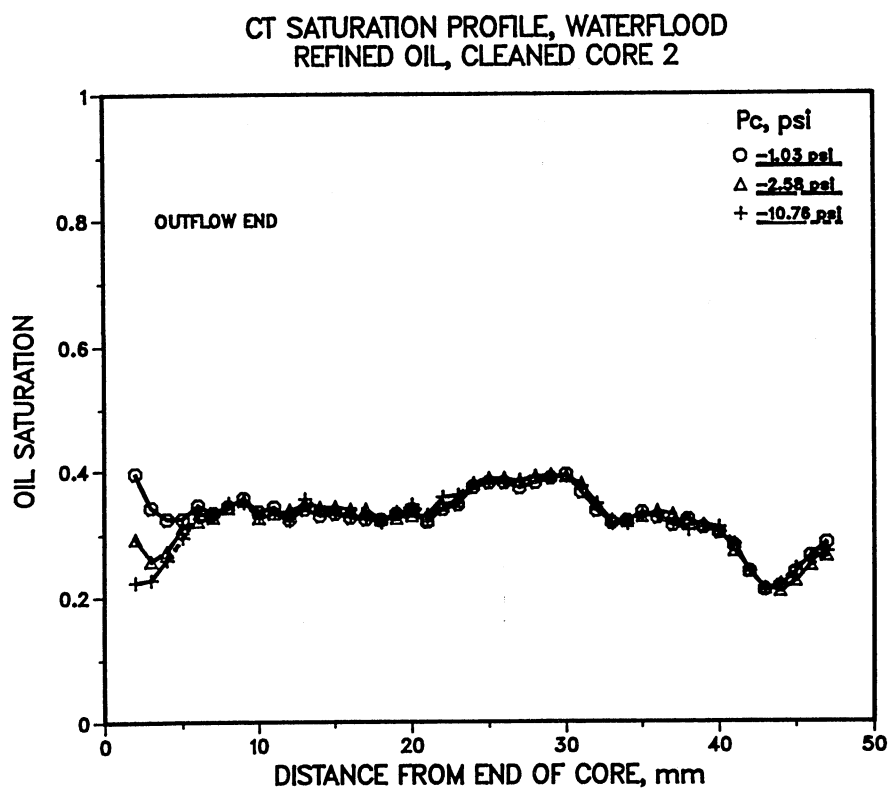


Fig. 15 – CT measured oil saturation during waterflooding to different negative capillary pressures; refined oil after third cleaning.

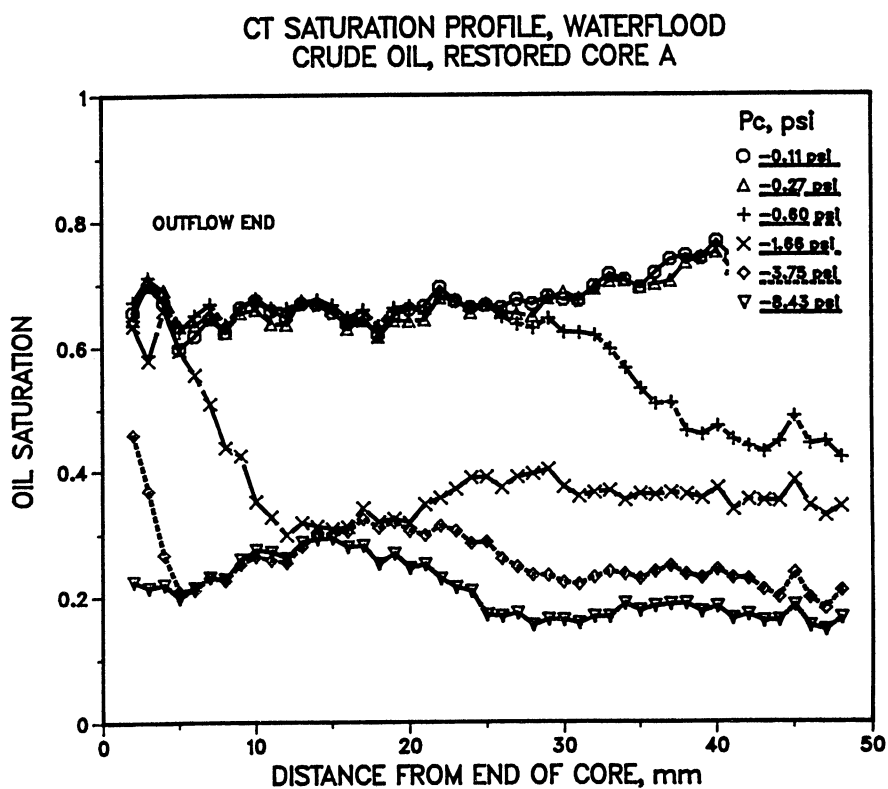


Fig. 16 – CT measured oil saturation during waterflooding to different negative capillary pressures; crude oil in core cleaned by Dean-Stark extraction and aged.

FILM DRAINAGE SATURATION PROFILE

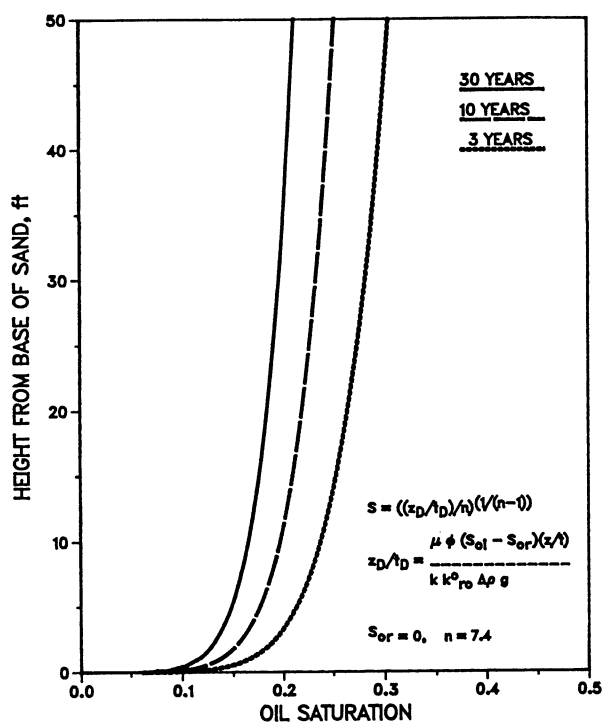


Fig. 17 – Remaining oil saturation distribution with gravity and film drainage.