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Obtaining Samples with Preserved Wettability

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I. INTRODUCTION

Wettability has a controlling influence on flow through an oil reservoir. Wettability affects the initial distribution of oil and water in the reservoir, and it helps determine on the microscopic level how much oil will remain when the reservoir's economic life is over. Any measurement that is performed to predict reservoir multiphase flow properties is meaningful only if the wettability of the sample tested is representative of the reservoir.

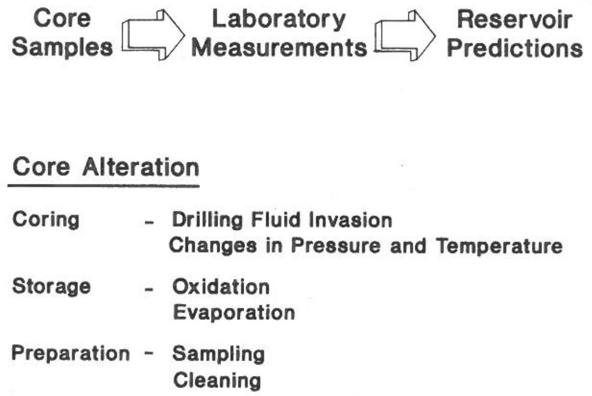

FIG. 1 Reliable reservoir predictions require unaltered core samples. Alteration can occur during coring, storage, and preparation.

The process of transferring a core sample from underground in the reservoir to the laboratory affords several possibilities for wettability alteration. As shown in Fig. 1, this process can be broken down into three steps:

1. Cutting core
2. Storing and transporting the core to the laboratory
3. Preparing samples for laboratory analysis

Wettability alteration is possible during any of these steps. This chapter will discuss why wettability alteration occurs and how it can be minimized.

II. CORING

Core alteration during coring can arise due to three effects: the coring process itself, interactions with drilling fluids, and pressure and temperature changes as the core is lifted to the surface. The coring process can lead to structural or mechanical damage. This will not be discussed in this chapter. Drilling fluid interactions and temperature and pressure changes can reduce permeability, damage clays, and change fluid saturations, in addition to altering wettability. Only the wettability effects will be discussed.

A. Wettability Alteration Due to Interactions with Drilling Fluids

The first chance for wettability to be altered occurs as the core is invaded by drilling fluid. Drilling fluid invasion will occur even for low filter loss drilling fluids because a clean surface with no filter cake is formed with each turn of the coring bit [1].

Drilling fluids have generally been designed for drilling a well as economically and safely as possible, and not for cutting undamaged cores [2]. Drilling fluids have several functions. They prevent inflow of formation fluids, transport cuttings, cool and clean the bit, reduce friction between the drill string and the hole, and maintain hole stability. Various additives are required to achieve drilling fluids with the desired properties, including surfactants, polymers, clays, bases, and inorganic salts. Some typical additives and their functions are listed in Table 1 [2, 3].

It has long been known that some of these additives could alter the surface properties of reservoir rocks. Bobek et al. [4] and Amott [5] studied various aspects of the wettability of oil reservoir rocks in the late 1950s, including the effects of drilling fluids on wettability. It is interesting to read these early articles, to see how many areas identified as key concerns are still being investigated today. Some of the details of their findings are described in Table 2. Their conclusions can be summarized as:

1. All of the oil-base and emulsion muds tested altered water-wet samples so that they became oil-wet or significantly less strongly water-wet. Quoting Bobek et al., "The results obtained with oil-base and oil-emulsion muds discouraged further investigation of these mud types"]4].
2. Water-base drilling fluids generally had only a small effect on water-wet samples. A few additives did reduce the degree of water-wetness.
3. Several of the components [carboxymethylcellulose (CMC), bentonite, and lime] in water-base muds reversed the wettability of oil-wet samples. These components were not necessarily the ones that would have had the largest effects on oil-wet samples—the more obvious surface-active agents had already been excluded by testing only those components that had no effect on water-wet samples.
4. Of the components tested, only rock salt and barite had no effect on either water-wet or oil-wet samples.

Despite these findings, it has been a common misconception in the oil industry that the best cores for core analysis are cut with oil-base drilling fluids. Such oil-base cores were often given the misnomer "native-state" cores, probably because it was believed that

TABLE 1 Examples of Additives Contained in Drilling Fluids

Function	Examples of additives
Bactericide	Paraformaldehyde, caustic, salts
Corrosion inhibitor	Amine salts, ammonium bisulfite
Defoamer	Surfactants, aluminum stearate
Emulsifier	Surfactants, lignosulfonate
Filtrate reducer	Bentonite, organic polymers, bentonite—polymer complexes, carboxymethylcellulose (CMC), xanthan gum, lignite
Flocculant	Surfactants, sodium tetraphosphate
Lost circulation control	Solids, cellophane, mica, calcium carbonate, paper, nut shells
Lubricant	Oils, graphite, surfactants
Pipe-freeing	Surfactants
pH Control	Caustic, bicarbonate
Shale inhibitor	Calcium lignosulfonate, gypsum
Thinner (mud conditioner)	Tanning (quebracho), polyphosphate, lignite, lignosulfonate
Viscosifier	Montmorillonite, polysaccharides, hydroxyethylcellulose (HEC)
Weighting material	Barite, calcium carbonate

Source: From refs. 2 and 3.

oil-base fluids maintained the original immobile water saturation in the core. This latter claim for oil-base fluids may or may not be true depending on surfactants in the oil-base fluid, but it is usually true that cores cut with oil-base fluids are not desirable for core analysis because of the likelihood of wettability alteration. This conclusion is based on personal experience as well as recent findings by Thomas [6], Cuiec [7], Yan et al. [8], and Yan and Sharma [9], which confirm and expand upon references 4 and 5.

Many in the oil industry have recognized the possibility of wettability alteration due to drilling fluids. It has become relatively standard for these parties to use what is called a "bland" water-base drilling fluid when making a special effort to minimize wettability alteration. In general, bland drilling fluids exclude surfactants and

TABLE 2 Wettability of Core Samples after Flushing with Drilling Fluids

Bobek et al. Data

Drilling fluid component	Initially water-wet limestone	Initially water-wet sandstone	Initially oil-wet sandstone
Rock salt	No change	No change	—
Starch	Slightly less water-wet	Slightly less water-wet	—
CMC	No change	No change	Water-wet
Bentonite	No change	No change	Water-wet
Tetrasodium pyrophosphate	No change	Less water-wet	—
Calcium lignosulfonate	No change	Less water-wet	—
Lime	No change	Slightly more water-wet	Water-wet

Amott Data

Drilling fluid type	Initially strongly water-wet sandstone	Initially weakly water-wet sandstone
High lime water-base	Slightly less water-wet	Less water-wet
Clay water-base	Slightly less water-wet	Less water-wet
Surfactant water-base	No change	Less water-wet
Oil-in-water emulsion	Weakly water-wet	Weakly oil-wet
Oil-base A	Moderately water-wet	Weak mixed wettability
Oil-base B	Moderately oil-wet	Moderately oil-wet

Source: Data from Bobek et al. [4] and Amott [5].

TABLE 3 Typical Specifications for a "Bland" Water-Base Drilling Fluid

Approved additives	Function
Clays	
Attapulgite	Gel strength
Bentonite	
Starches and polymers	
Starch	Filter loss control
Dextrid	
Carboxymethylcellulose (CMC)	
Hydroxyethylcellulose (HEC)	
Drispac	
Xanthan gum	
Inorganic salts	
Calcium chloride	Salinity control
Sodium chloride	
Potassium chloride	
Weight control	
Barium sulfate (barite)	
Calcium carbonate	
Bactericide	
Formalin (formaldehyde and methanol)	
Desired Properties	
Less than 10 cm^3/30 min API filter loss	
pH 7–9	
Low solids content	
Excluded additives	
All surfactants including:	
Defoaming agents	
Dispersants	
Emulsifiers	
Deemulsifiers	
Thinners	
Lubricants	
Corrosion inhibitors	
Lignosulfonates	
Bactericides (except formalin)	
All acids except hydrochloric	
All bases except for small enough quantities such that pH < 9, including:	
Caustic (lye, sodium hydroxide)	
Soda ash (baking soda, sodium bicarbonate)	

Source: Ref. 10.

restrict the pH to a narrow range close to neutral [10–12]. Typical specifications for a bland drilling fluid are listed in Table 3 [10]. It is interesting to note that several of the components allowed in a bland fluid are similar or identical to the components found by Bobek et al. [4] to alter oil-wet samples. Perhaps these components were allowed because of the widespread assumption that most reservoirs were water-wet, so that drilling fluids that did not alter water-wet samples could be considered bland. With the growing acceptance of a broad range of reservoir wetting properties, bland drilling fluids must satisfy a tougher standard.

Sharma and Wunderlich [10] tested many of the components allowed in bland drilling fluids to determine if they were in fact bland. The effects on both water-wet and oil-wet samples were considered by contact-angle measurements and a combined USBM/Amott capillary pressure type wettability test. Clean quartz and calcite crystals were used as water-wet surfaces for the contact-angle tests, and asphaltene films deposited on glass microscope slides were used as oil-wet surfaces. Fired Berea sandstone samples and Berea sandstone samples that had been treated with asphaltenes were used as water-wet and oil-wet samples, respectively, for the combined USBM/Amott wettability tests. The asphaltene-treated Berea sample actually had a mixed wettability, freely imbibing small amounts of water in addition to larger amounts of oil.

Some of the contact-angle data are shown in Figs. 2 and 3. The blank samples were not contacted with drilling fluid components. The other samples were contacted with the stated drilling fluid component and then rinsed with deionized water. Figure 2 illustrates that the bland components did not have a significant effect on the wettability of clean quartz crystals. Coat 415, a cationic amine, reversed the wettability of these crystals, but Coat 415 would generally be excluded from a "bland" drilling fluid. Much more dramatic effects were found with the oil-wet surfaces. As shown in Fig. 3, all of the bland components with the possible exception of bentonite

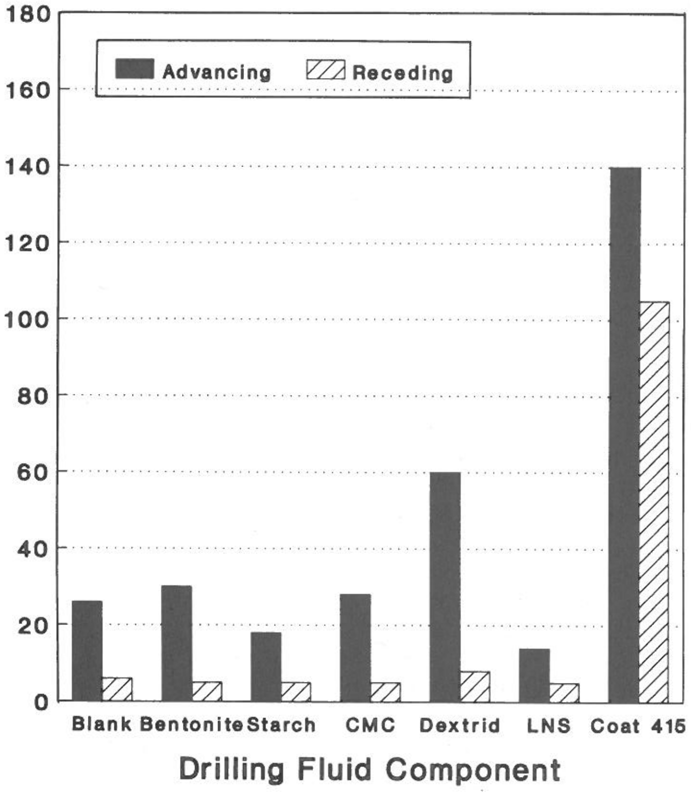

FIG. 2 Contact angle data indicate that bland components have little effect on the wettability of quartz crystals. (From Ref. 10.)

filtrate made the oil-wet surface less strongly oil-wet or even water-wet.

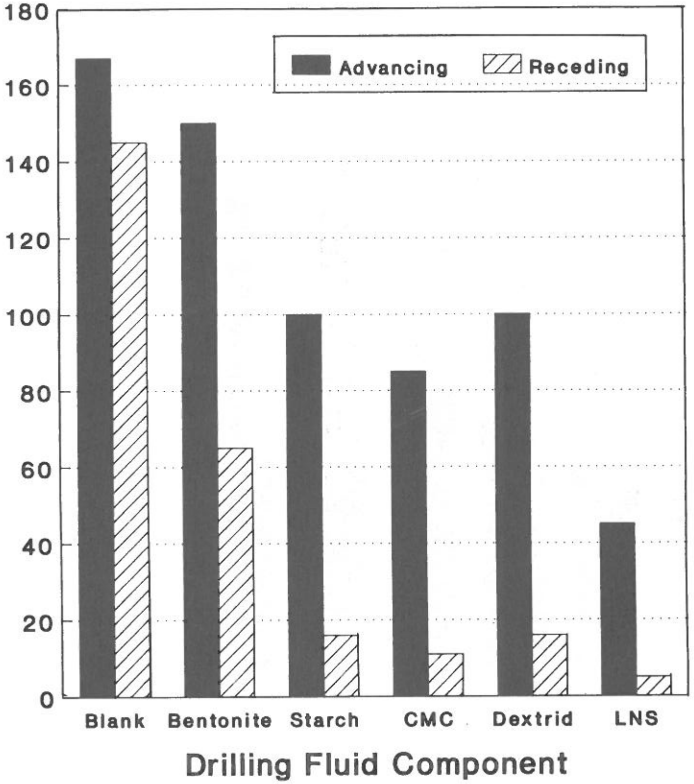

FIG. 3 Most bland components had a significant effect on the wettability of asphaltene films. (From Ref. 10.)

The USBM/Amott wettability tests confirmed the contact-angle data, although the rock capillary characteristics were generally less sensitive to change than contact angles on smooth surfaces. Data for the water-wet samples are shown in terms of Amott ratios in Fig. 4. The closer the Amott ratio is to one, the stronger the wetting tendency. In performing these tests, two or three samples of the same wettability were butted together and flushed simultaneously to give an indication of depth of alteration. The bars in the figures are ordered such that for a given component the left-most bar corresponds to the upstream sample. As with the contact-angle tests, only Coat 415 had a significant effect on the water-wet samples. Data for the predominantly oil-wet samples are presented in Fig. 5 in terms of the ratio of the water Amott index to the oil Amott index. This was found to be more sensitive than the oil Amott index by itself. Again, as with the contact-angle tests, all the bland components with the exception of bentonite filtrate made the samples significantly less strongly oil-wet. The effect was generally greatest in the upstream sample, when indicated a limited depth of invasion. Lignosulfonate (LNS) reduced both water and oil imbibition, but LNS would normally be excluded from a bland drilling fluid.

The wetting effects of eight whole drilling fluids were also tested. The response of a whole drilling fluid is difficult to predict from the behavior of its individual components because of interactions among the components and the formation of filter cakes, which reduce invasion. The compositions of the fluids tested are listed in

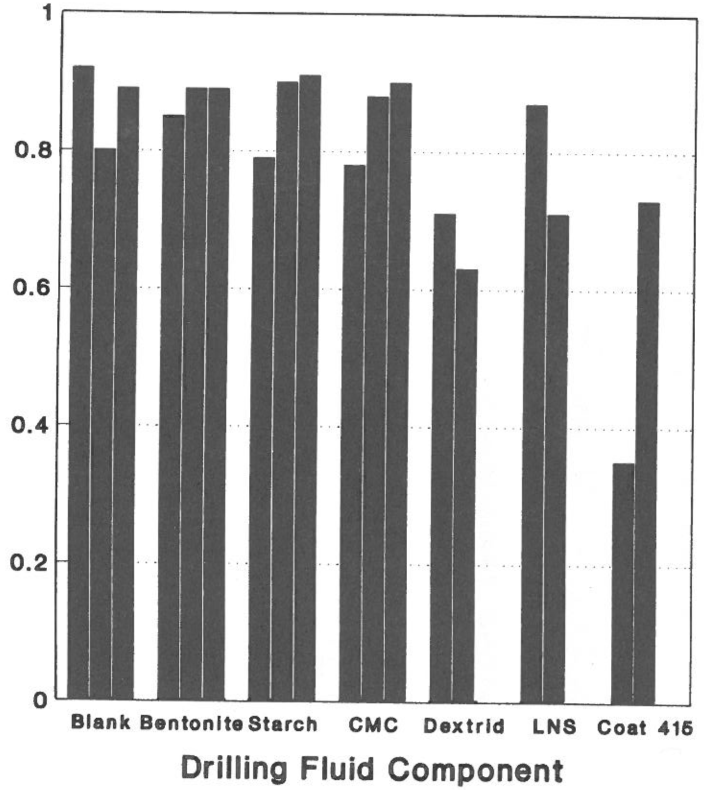

FIG. 4 Amott ratios indicate that bland components have little effect on water-wet samples. Coat 415, a filming amine, does have an effect. The figure is drawn such that the bar furthest to the left in each group corresponds to the upstream sample. (From Ref. 10.)

Table 4, and imbibition data for the water-wet and oil-wet samples are in Figs. 6 and 7. The whole drilling fluids generally had less of an effect than the individual components, but some did make the oil-wet samples significantly less strongly oil-wet. The largest effects were found for those drilling fluids that lacked components to form a good filter cake or that contained especially damaging components.

Yan et al. [8] and Yan and Sharma [9] used a similar format to study components in oil-base drilling fluids and whole oil-base drilling fluids. These components would generally be excluded from a "bland" drilling fluid, and indeed all of the components were found to reduce or reverse the wetting tendencies of water-wet samples.

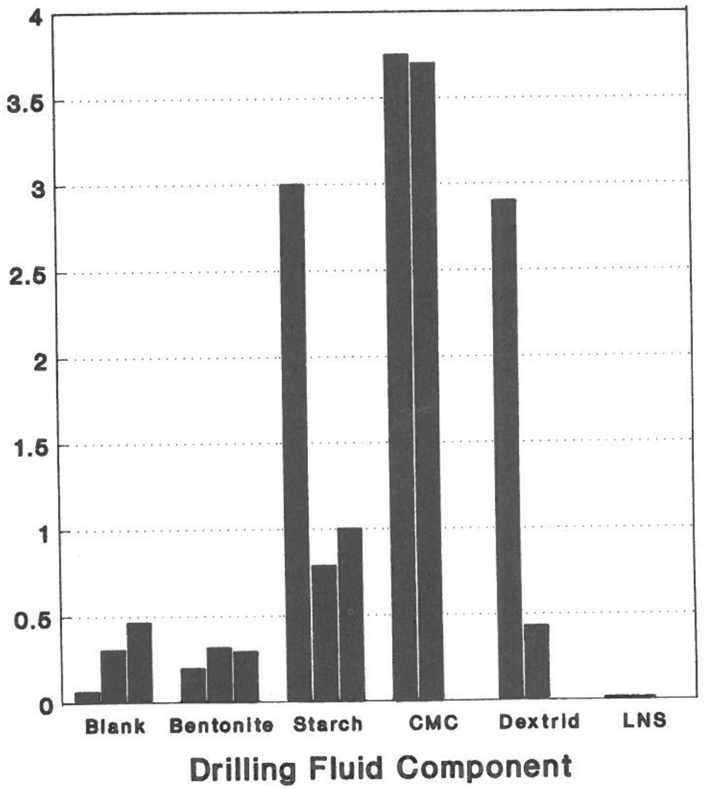

FIG. 5 Dividing the water Amott ratio by the oil Amott ratio illustrates significant effects on oil-wet samples due to bland components. The data also suggest that alteration decreases with distance from the upstream end. The upstream sample corresponds to the bar that is furthest to the left in each group. (From Ref. 10.)

The base oils themselves had much smaller effects. Examples of their Amott wettability data are given in Fig. 8. Cuiec [7] has also studied oil-base, water-base, and "bland" water-base whole drilling fluids with similar results.

Many of the tendencies to alter wettability observed in these studies can be understood in terms of the effects of adsorption and surface charge modification on the stability of wetting films [10, 13]. This is discussed at length in Chapter 2 of this book. For now, consider the case of a water film separating oil from a solid surface. If the solid/water interface has the same sign of charge as the oil/water interface, then electrostatic repulsion will promote the stability

TABLE 4 Composition of Whole Drilling Fluids

Component	Drilling fluid composition (pounds per barrel)							
	1	2	3	4	5	6	7	8
KCl	7.00	10.5	10.5	10.5	10.5	10.5	10.5	10.5
KOH	0.56	0.40	0.50	0.50	0.50	0.50	0.50	0.50
XCD	—	0.80	0.70	0.70	0.70	0.70	0.70	0.70
Gel	8.90	—	8.00	8.00	8.00	8.00	8.00	8.00
$CaCO_3$	48.9	60.0	15.0	50.0	50.0	50.0	50.0	50.0
Drispac	—	1.00	1.00	1.00	1.00	1.00	—	—
Benex	0.34	—	—	—	—	—	—	—
WL-100	0.56	—	—	—	—	—	—	—
Barite	—	—	30.0	—	—	—	—	—
Soltex	—	—	—	—	4.00	—	—	—
Shale-Tone	—	—	—	—	—	4.00	—	—
Mineral oil	—	—	—	—	—	—	4.00	—
Proctectomagic	—	—	—	—	—	—	—	4.00

Source: From Ref. 10. Fluids and data supplied by Hughes Drilling Fluids.

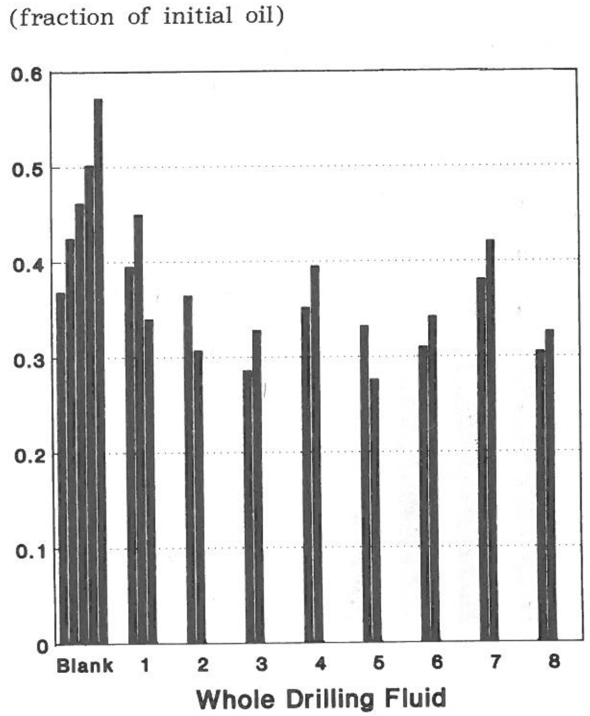

FIG. 6 Whole drilling fluids tested did not have a significant effect on imbibition in water-wet samples. (From Ref. 10.)

of the wetting film. If the two interfaces are oppositely charged, and if only electrostatic forces are considered, then the film will be unstable and will drain.

Starches were among the components found to alter oil-wet surfaces. Untreated starches are anionic, and impart a negative charge to the surfaces on which they absorb. Since the oil/brine interface is also negatively charged under reservoir conditions, the absorption of starch will tend to make solid surfaces hydrophilic by stabilizing water films. In fact, starches are known from the flotation literature to absorb on hydrophobic mineral surfaces, reversing wettability. Similarly, cationic substances can impart a positive charge to mineral surfaces. This would tend to destabilize aqueous wetting films. This has been observed in the past during contact-angle measurements using oil phase doped with organic amines, and was also observed during drilling fluid studies with Coat 415.

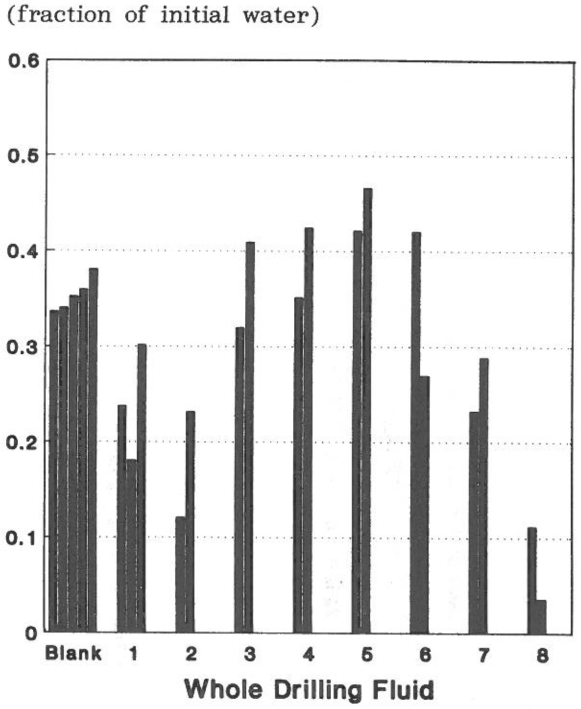

FIG. 7 Some of the whole drilling fluids significantly reduced oil imbibition in the oil-wet samples. (From Ref. 10.)

Based on the drilling fluid studies, one can rank drilling fluid types in terms of how likely they are to alter wettability. My own list in order of increasing likelihood follows. Drilling fluid types grouped at a single numerical rank are judged to be similar. Any reservoir fluid samples are assumed to be stable, properly filtered, and protected against oxidation. A large jump is believed to occur between number 3, a "bland" drilling fluid, and number 4, a routine drilling fluid.

(Least likely)

1. Reservoir or synthetic reservoir brine
   Reservoir crude oil
2. Water-base fluid (close to neutral pH) containing only inorganic salts and bentonite
   Refined oil with no additives
3. Water-base fluid with inorganic salts, bentonite, starches, and polymers (as described in Table 3)

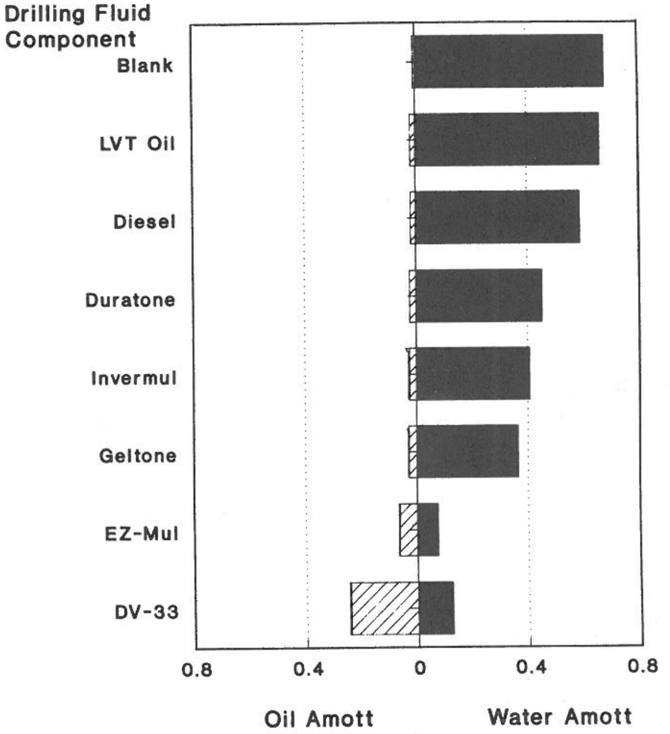

FIG. 8 Oil-base drilling fluid components tended to make water-wet samples less strongly water-wet or oil-wet. (From Ref. 8.)

4. Routine water-base fluid
   Low-surfactant oil-base fluid
5. Routine oil-base fluid
   (Most likely)

Selecting a drilling fluid for coring involves considering the uses for the core and any constraints imposed by drilling concerns. If preserving wettability is critical, then the drilling fluid that is ranked highest on the list and is feasible from a drilling point of view should be used. Drilling considerations often, but not always, rule out using options 1 and 2 above, so that option 3, a "bland" drilling fluid, is selected.

If a drilling fluid that does have the potential for altering wettability is used, then drilling fluid invasion should be minimized. Invasion can be reduced by increasing penetration rate, decreasing overbalance pressure, reducing filter loss, and cutting a larger-diameter core.

FIG. 9 Schematic of experimental set-up to study asphaltene deposition in a capillary tube. Over time, propane diffuses through the brine into the crude oil, destabilizing asphaltenes. (From Ref. 16.)

B. Pressure and Temperature Changes

Pressure and temperature in the core drop from reservoir to atmospheric conditions as the core is raised to the surface. Fluids will be expelled by gas evolution as the pressure is lowered, but the most significant impact from the point of view of wettability alteration is the possible destabilization of the oil phase. Both asphaltenes and waxes can separate from the oil phase as pressure and temperature are changed [14, 15]. These effects are widely recognized to have a major impact on wettability, but little has been done to quantify the effects or to develop remedies.

A set of interesting experiments has recently been performed by Yeh [16]. These experiments were designed to study asphaltene deposition accompanying miscible EOR floods, but some of the physical phenomena are similar to those that occur when a core is lifted to surface. In the experiment, slugs of crude oil and propane in a quartz capillary tube are separated from each other by a slug of brine, as shown in Fig. 9. The contact angles at the brine/crude oil and brine/propane interfaces are initially close to zero. Over time, propane diffuses through the brine into the crude oil, raising the relative amount of light hydrocarbon in the oil phase. At some point the asphaltenes in the crude oil become unstable, leaving a clearly visible residue on the quartz surface. The contact angle at the brine/crude oil interface becomes greater than 90°.

Analogously, as a core is being lifted to the surface, the oil phase becomes closer and closer to being saturated with light hydrocarbons, until eventually gas comes out of solution. Asphaltenes could become unstable at a critical saturation, leading to alteration of the core. Yeh has attempted to study asphaltene deposition induced simply by pressure reduction, but so far has been unsuccessful, largely because of the difficulty of obtaining an appropriate crude oil sample. What is needed is an asphaltic sample that is stable at reservoir pressure but becomes unstable as the pressure is lowered. This requires working with a bottom hole sample, since any sample captured at the surface will have already become unstable. Adding asphaltenes back to a surface sample and returning the mixture to reservoir conditions usually is not a successful means of creating a suitable sample.

Yeh's work is a step toward determining what can be done if asphaltene deposition does occur. The timing of wettability alteration is critical. If the alteration is slow to occur, then tests performed as quickly as possible may provide reliable information. Remedial actions could also be most effective if minimum time is provided for the alteration to become lasting. Perhaps we should immediately (at the well site) replace the oil in the core with a stable oil phase or return the core sample to reservoir conditions. Some evidence that wettability alteration does occur after the core reaches the surface and so at least that part of the alteration would be avoidable is discussed below. Experiments similar to those of Yeh will provide a way to study the dynamics of alternation and the effectiveness of remedial procedures.

III. STORING

Once the core gets to the surface it must be protected against evaporation, oxidation, and contamination. Whatever method is used to preserve the core, it should be applied quickly. Significant drying can occur in tens of minutes. Any well-site core examination should be brief. If the core is intended for wettability-sensitive tests, then detailed well-site core descriptions should be avoided. If the core is examined at the well site, it can be protected by submerging it under brine in troughs.

The brine used at the well site as well as in any core preservation method would preferably be a synthetic reservoir brine. At a minimum, the brine should be chosen so that it will not damage clays. A bactericide should be added to the brine if the samples are to be stored for an extended period.

Four popular methods for preserving core are described below and in Table 5.

1. ProtecCore. The core is first wrapped with Barex film, a transparent, chemically resistant polymer. The wrapped core is placed in a tubular-shaped laminated material, containing layers of aluminum, polyethylene, and polyester. The tubular wrapping is sealed with a heat sealer. Plastic bubble wrap can be placed around the core to guard against mechanical damage during shipping.

It has been informally reported that ProtecCore has a tendency to crimp and tear if not handled carefully. Some workers like to use a vacuum to exclude air and insure a tight fit between ProtecCore and the core. This practice is not personally recommended because it increases the tendency for the material to tear. The ProtecCore method requires considerable handling of the core, so that

TABLE 5 Comparison of Core Preservation Methods

	ProtecCore	Core Seal	Submerge under fluid	Plastic liner
Evaporation protection	Good	Good	Good	Fair
Wettability alteration protection	No clear advantage for any method			
Required handling of core	High	High	High	Low
Ease of shipping	Medium	High	Low	High
Accessibility of core on-site	High	High	High	Low
Ease of opening and resealing core	High	Medium	Low	Medium
Suitability for unconsolidated or extensively fractured core	No	No	No	Yes
Resistance to deterioration due to contact with crude oil	High	Sometimes low	High	Medium

Source: Based on subjective opinion of author and studies reported here and in refs. 17 and 18.

it is not suitable for unconsolidated or extensively fractured formations.

2. Core Seal. The core is wrapped with multiple (seven to eight) layers of Saran Wrap followed by aluminum foil, and coated with a molten strippable plastic. Saran Wrap is relatively inert, but in some cases it has been found to interact with the crude. If its integrity is lost, then aluminum foil can potentially interact with brine in the core, especially if a high-pH drilling fluid had been used. Core Seal offers a superior barrier against evaporation compared to an earlier similar product, Seal Peel. Core Seal involves considerable handling of the core and is not suitable for unconsolidated or extensively fractured formations. Once the core has been packaged, it is very easy to handle and transport.

3. Submerge in brine or crude oil. The core is placed in PVC cylinders or other plastic container, and is submerged in deoxygenated brine or unoxidized reservoir crude oil. Metal cans have also been used for this in the past, but corrosion can be a problem. If crude oil is used, ensure that the plastic container does not interact with the crude oil. A nitrogen cap is sometimes placed over the preserving fluid. The common practice of using drilling fluid instead of brine as a preserving fluid is not recommended because of possible alteration due to interactions with drilling fluid components. Considerable handling of the core is required and the method is not suitable for unconsolidated or extensively fractured formations. The sealed fluid-filled tubes can be messy to open to access the core, and the combined weight of the fluids and the rock can make the tubes relatively difficult to handle. The method does provide excellent protection against evaporation as long as the samples remain submerged.

4. Plastic-inner-liner core barrel. The core is cut using a plastic-inner-liner core barrel. The inner liner is pulled from the barrel, cut into three foot sections using pipe cutter, and tightly capped. Sponge-core inner liners also work with the method. This is an excellent method for unconsolidated or fractured formations, since minimal handling of the core is required. The tubes also lend themselves quite well to shipping and handling. The trade-off is that the core is difficult to examine. Only the ends of the three-foot sections can be viewed at the well site. For unconsolidated or fractured formations, the annular space between core and plastic liner can be filled with a fast-setting plastic to maintain mechanical integrity of core during shipping and handling, although this may have deleterious effects on wettability preservation.

A few studies of the effectiveness of different core preservation techniques have been performed. Auman [17] compared different strippable plastics and plastic laminates in terms of preventing evaporation. Berea sandstone samples (1 in long by 3/4 in diameter) were saturated with brine and packaged in one of the preserving materials. Evaporation was monitored by weighing the samples without removing the packaging material. Polypropylene/aluminum laminates were found to be superior to any of the strippable plastics (identified only as types A, B, and C). Evaporation losses were approximately 0.013% of pore volume in 40 days. The best strippable plastic, even without inner layers of plastic wrap and aluminum foil, was also effective, limiting evaporation to approximately 0.11% of pore volume in 40 days.

We have performed a similar comparison of ProtecCore and Core Seal. We used larger samples (4 in long by $1\frac{1}{2}$ in diameter) and we monitored saturation changes both while the samples were still inside the packaging material and after removing the samples. This last comparison proved to be revealing. A significant amount of fluid was found to have evaporated out of the samples but remain trapped within the packaging material. Our results are given in Table 6. Evaporative losses in 130 days for ProtecCore averaged 0.06% of pore volume for samples still in the packaging material and 2.98% for the samples after they were removed from the packaging. Evaporative losses in 130 days for Core Seal averaged 0.078% of pore volume for samples still in the packaging material and 0.65% for the samples after they were removed from the packaging.

Our results for the ProtecCore samples still in the packaging are roughly similar to Auman's results for his laminated material. However, our tests indicate a poorer ultimate performance because of the fluid found to be trapped in the packaging material. This could perhaps have been reduced by minimizing the amount of trapped air before sealing the ProtecCore, as Auman recommends in his paper, although this could increase the likelihood of crimps and tears. Our results for Core Seal samples still in the packaging indicate a superior performance compared to what Auman found for his best strippable plastic. This could be because we included inner layers of plastic wrap and aluminum foil, which were omitted by Auman. Overall, both our and Auman's work indicate that laminated materials and strippable plastics (especially with inner layers of plastic wrap and aluminum foil) can be effective evaporation barriers.

Neither of these studies modeled the effects of crude oil in the core samples. Hunt and Cobb [18] did perform a comparison of laminated materials and B-60 Hot Melt Peel Coat Type II in which the core samples contained both water and oil. The laminated material was found to be superior in terms of both evaporation prevention and chemical resistance. After 2 years of storage, the inner layers of plastic wrap and aluminum foil used with the strippable plastic exhibited significant deterioration, whereas the laminated material appeared intact. Evaporative losses were as high as 80% for the strippable plastic and less than 10% for the laminated material.

In order to evaluate the preservation techniques in terms of preventing wettability alteration, a baseline wettability must be determined as quickly as possible after the core reaches the surface. Bobek et al. [4] performed well-site imbibition tests on fresh core samples from two reservoirs and preserved additional samples by immersion in deoxygenated brine or packaging with polyethylene film, Saran Wrap, and paraffin. Eight months later they determined that both methods had satisfactorily preserved the water imbibition characteristics of the fresh core.

TABLE 6 Comparison of ProtecCore and Core Seal as Evaporation Barriers

Sample	Pore volume (ml)	Saturation change (% pore volume) in 130 days	
		Still in packaging	After removing packaging
ProtecCore			
P1	36.50	0.05	2.05
P2	36.11	0.03	1.83
P3	36.39	0.08	2.17
P4	36.24	0.00	3.64
P5	36.49	0.05	2.47
P6	35.95	0.06	1.78
P7	33.69	0.09	2.40
P8	33.65	0.06	2.05
P9	33.67	0.09	2.64
P10	34.55	0.09	2.52
P11	34.62	0.14	2.66
P12	34.20	0.00	0.92
P13	34.66	0.03	3.09
P14	33.88	0.06	2.69
P15	33.84	0.00	2.66
P16	34.78	0.00	3.31
P17	34.85	0.09	4.05
P18	33.72	0.03	3.94
P19	34.19	0.15	4.83
P20	34.59	0.12	5.81
Mean	34.83	0.06	2.98
SD	1.05	0.05	1.04
Core Seal			
C1	36.00	0.08	0.56
C2	36.86	0.08	0.62
C3	36.90	0.08	0.41
C4	36.33	0.06	0.44
C5	36.71	0.08	0.65

TABLE 6 (Continued)

Sample	Pore volume (ml)	Saturation change (% pore volume) in 130 days	
		Still in packaging	After removing packaging
Core Seal (continued)			
C6	36.49	0.05	0.55
C7	33.14	0.06	0.48
C8	33.81	0.09	0.44
C9	33.86	0.03	0.53
C10	34.24	0.06	0.70
C11	34.33	0.06	0.84
C12	34.62	0.12	0.95
C13	33.91	0.12	0.53
C14	33.58	0.09	0.80
C15	33.59	0.06	0.80
C16	34.01	0.09	0.74
C17	33.19	0.09	0.87
C18	33.84	0.09	0.65
C19	33.42	0.12	0.78
C20	33.87	0.07	0.53
Mean	34.64	0.08	0.65
SD	1.34	0.02	0.16

We have also performed similar comparisons for several reservoirs. Results are given in Figs. 10 and 11. Immersion in brine was an effective preservation method for one high-permeability (500 md) sandstone reservoir. The fresh core and core preserved for approximately 6 months were similarly weakly water-wet. After extraction, the same cores were strongly water-wet. No method was satisfactory for a second, low-permeability (< 10 md) sandstone reservoir with an asphaltic crude oil. The fresh cores had a definite mixed wettability, freely imbibing either oil or water when predominantly saturated with the opposite phase. Core samples were preserved by three techniques: Core Seal, immersion in crude oil, and immersion in brine. Two years later the samples were entirely oil-wet. Not one imbibed any water.

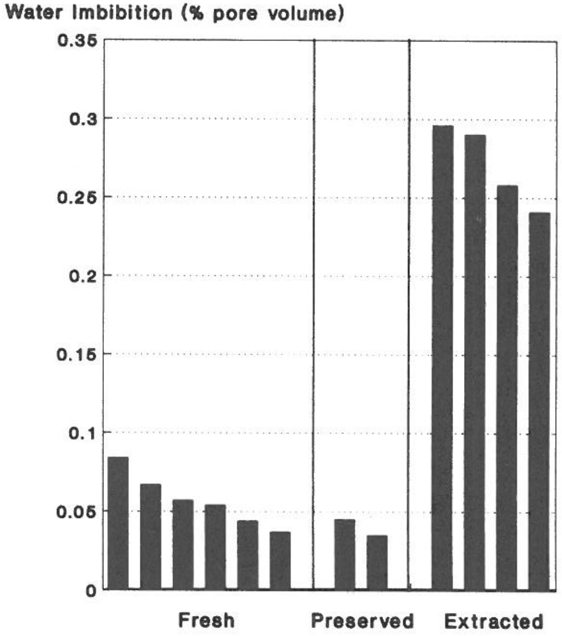

FIG. 10 The weakly water-wet character of sandstone reservoir A was preserved by submerging the core in brine. Examples of six fresh, two preserved, and four extracted samples are shown.

There are at least two significant aspects to the alteration observed in the second case. The first is that asphaltene deposition is a likely cause of the alteration. None of the preservation methods provides protection against such deposition. The second is that alteration continued after the core reached the surface. We have no way to compare down-hole wettability with surface wettability, but we do know that the samples lost all traces of water wetting after they were tested at the surface.

Tests with a high-permeability reservoir with a paraffinic crude oil [19] also provide information concerning the time scale over which alteration occurs. Qualitative wettability tests were performed on the core as soon as it reached the surface. The core appeared to be water-wet. Within 24 hours, the core samples became oil-wet.

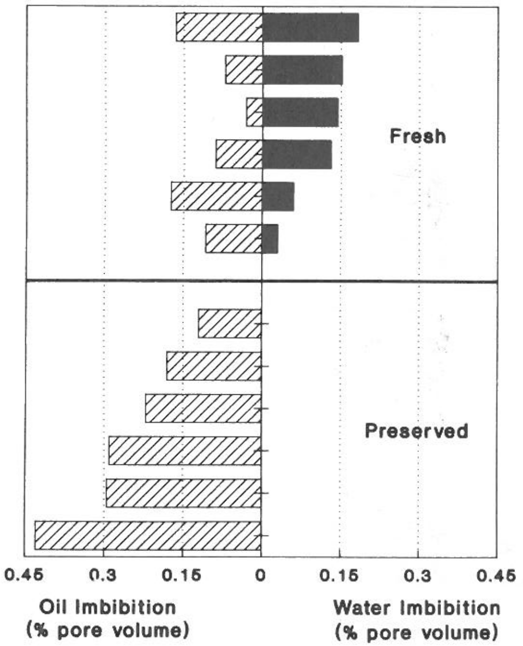

FIG. 11 The mixed wettability of sandstone reservoir B was not preserved by any of three core preservation techniques. Examples of six fresh and six preserved samples are shown.

The experience with these two reservoirs suggest that problems due to asphaltene or wax deposition can be mitigated if action is taken as quickly as possible. If asphaltene or wax deposition is suspected, then tests should be performed immediately or the oil phase should be replaced with a stable oil phase.

IV. LABORATORY PREPARATION

Even after the core sample reaches the laboratory, its wettability can be altered by the methods used to prepare it for laboratory tests. Some methods can obviously affect wettability. Hot extraction should be avoided due to the potential for making samples more water-wet by removing naturally absorbed organics or more oil-wet by removing water but not the heavy ends of crude oil. Drying samples should also be avoided.

Preserved core plugs should be cut from the bulk core using a synthetic formation brine as the cutting fluid, unless other factors make this not practical. Samples that are very susceptible to clay damage can be cut using a clean oil that has been found to have no adverse interactions with the field crude oil. Unconsolidated cores should preferably be cut using a core punch on a carefully supported core. Fractured cores and unconsolidated cores can also be cut with liquid nitrogen if necessary to maintain the physical integrity of the samples.

There are at least four schools of thought regarding how core samples should be cleaned. They can be described as:

1. No solvents
2. Clean and restore
3. Avoid hysteresis
4. Clean without restoring

The last method is not a serious attempt to maintain wettability, although it is frequently used. It will be effective only if the natural wettability happens to be similar to the wettability after cleaning. Its advantage is that it is convenient and cheap. The other three methods will be discussed below.

A crucial step for all of these methods is establishing a representative initial water saturation. There are two difficulties here: knowing what a representative initial water saturation is, and attaining that water saturation in the core sample. Resolving the first problem requires additional information, perhaps from capillary pressure measurements or well logging. Resolving the second requires experimental care. Various techniques have been used to establish the desired water saturation, including oil flooding, centrifugation, and desaturation using a water-wet semipermeable membrane. It is often necessary in the oil flooding method to flood for many pore volumes, or to first flood with a viscous oil and then replace that oil with the desired test oil.

A. "No Solvents" Procedures

The "no solvents" procedures derive from concerns regarding the effects of solvents on altering naturally existing wetting conditions. Advocates of "no solvent" are skeptical that samples can be cleaned and then restored to their reservoir wettability because of the uncertainty regarding and difficulty duplicating reservoir conditions, including reservoir fluids, pressure and temperature history, and time.

Typical "no solvents" preparation begins with preserved core samples that were cut with a water-base "bland" drilling fluid. Initial water saturation is established by flushing (against back pressure to remove gas) the core samples with synthetic reservoir brine followed by reservoir crude oil (most commonly a dead, unoxidized sample). Experiments are usually performed at reservoir temperature and possibly pressure. A disadvantage of this approach is that pore volume and saturation cannot be known until the conclusion of the measurements.

B. "Clean and Restore" Procedures

Proponents of the "clean and restore" procedures argue that core samples at the surface are likely to have been altered due to drilling fluid invasion, pressure and temperature changes, oxidation, evaporation, or contamination. They believe that instead of using preserved core, it is better to clean the samples thoroughly and then simulate the processes by which the samples achieved their reservoir wettability [20].

Typical "restoration" procedures preferably begin with preserved core, but can also be applied to nonpreserved core. The cores are vigorously cleaned by flushing (usually at room temperature at slow flooding rates) with repeated cycles of several solvents such as toluene, methanol, chloroform, and acetone. Acids and bases are also sometimes used. The goal is to return the samples to their wetting condition (presumably water-wet) before crude oil entered the reservoir. The samples are then saturated 100% with synthetic reservoir brine. (This can be accomplished without drying the sample or precipitating salts from the brine if the last solvent used is methanol, and the brine is introduced gradually by flowing with methanol/brine solutions of increasing brine fraction, finally ending with 100% brine.) Initial water saturation is established by displacing brine with reservoir crude oil. The samples are then aged at reservoir temperature and possibly pressure. The aging time can be arbitrary (1000 hours is a popular number) or based on sample-specific aging studies in which the apparent time beyond which no wettability changes occur has been determined.

C. "No Hysteresis" Procedures

The "no hysteresis" procedures are designed to maintain the history of fluid displacements in the sample. Water was initially the only liquid in the reservoir. Oil migrated in displacing water. The reservoir could possibly have naturally acquired some oil-wetting tendencies for a variety reasons (absorption of organics, particular brine and surface charge conditions, solid hydrocarbon material, etc.), but it is likely that the initial water has remained in a water-wet configuration. Any new water introduced into the sample (from drilling fluids, reservoir waterfloods, laboratory flushing) has to displace oil. This water could enter in an oil-wetting configuration because of wettability hysteresis. If so, it may not be possible to return the sample to its initial configuration of fluids without going through the clean and restore process [21].

The "no hysteresis" procedures preferably begin with a sample that was cut with an oil-base drilling fluid (presumably one with no surfactants) so that no new water had been introduced. The drilling fluid oil is then displaced with the experimental oil, and the sample is already at initial water saturation and is ready to start the experiment. If the samples had been cut with a water-base mud, then clean and restore procedures would be used.

D. Recommendations for Cleaning Procedures

There is no convincing evidence that demonstrates the clear superiority of one set of procedures. It appears likely that the best method will be sample specific in a way that will be difficult to predict in advance. The "no cleaning" procedures fail if the core has been altered or if hysteresis is significant. The "clean and restore" procedures avoid hysteresis effects, but fail if reservoir history has not been matched. (Are today's surface crude oil samples the same as the oil that established reservoir wetting conditions? Have hydrocarbon absorbents been removed that are not replaced by restoration? Are slowly occurring processes captured by the aging period?) The "no hysteresis" procedures beginning with an oil-base core are subject to the likelihood of alteration due to drilling fluid invasion. The procedures beginning with a water-base core amount to the same as the "clean and restore" procedures.

The optimal procedure given this uncertainty is to do measurements by both the "no cleaning" and "clean and restore" methods. If they agree, then much confidence can be placed in the results since they were arrived at by different approaches. If they disagree, then at least a range of possible behavior has been determined. If cost or timing constraints limit the number of measurements, and if preserved core is available, then the "no cleaning" procedures are recommended for wettability tests. If preserved core is not available, then the "clean and restore" procedures must be used.

It is often desired for special core analysis to clean samples by more convenient procedures than those specified here. (For example, the analysis is simpler if the sample is cleaned so that it starts out 100% saturated with brine, and the time or cost of length aging may be prohibitive.) The wettability of more conveniently cleaned samples can be compared with baseline wettabilities derived from "no solvents" or "clean and restore" procedures. If there is good agreement, then confidence can be placed in measurements performed with the easier cleaning procedures.

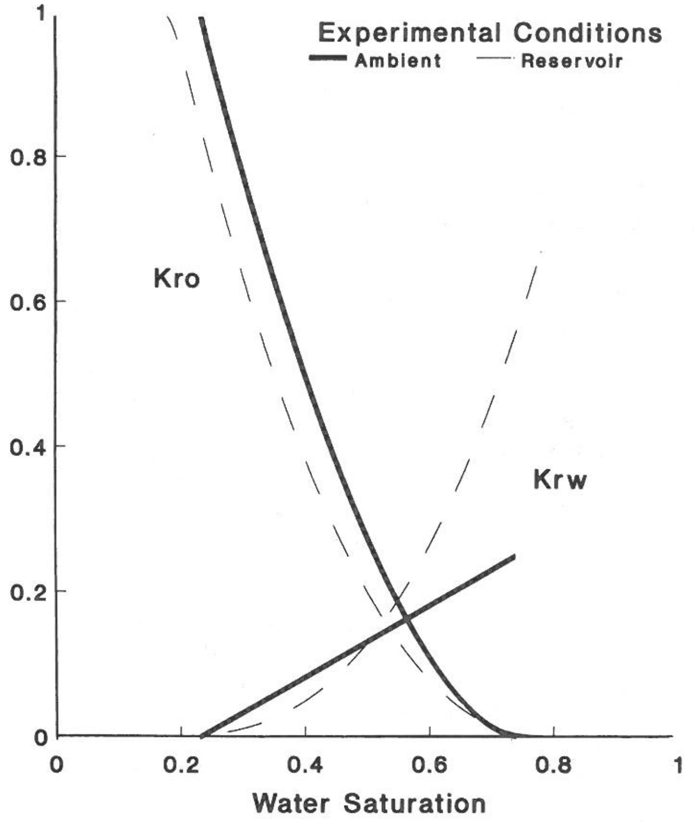

FIG. 12 Relative permeability curves for a high-permeability sandstone reservoir. Relative permeability and residual saturations were sensitive to experimental conditions. (From Ref. 23.)

E. Experimental Conditions

A second area of some controversy in performing laboratory measurements is whether they should be performed at reservoir conditions. Certainly the chemistry and physics of wetting suggest that the specifics of fluids and thermodynamic conditions can affect wetting behavior [13, 22]. In addition, many instances have been reported where the results at reservoir conditions differ from those at laboratory conditions using refined oil. One example from our files of the variation of waterflood behavior in terms of residual oil saturation and relative permeability is provided in Fig. 12 [23]. Other examples can be found in references 24 and 25. Given theoretical and experimental evidence, the burden of proof must fall on those who wish to do room-conditions experiments. They must demonstrate for each specific reservoir that the room-conditions results are similar to the more difficult-to-perform reservoir-conditions tests.

V. CONCLUDING REMARKS

Much of this book is devoted to understanding and predicting oil reservoir behavior based on wettability. One essential aspect of this difficult problem is characterizing and obtaining samples with the native wettability. This chapter has not been able to offer a prescription that can guarantee accomplishing this, but it is hoped that it has described procedures that will minimize alteration based on present knowledge, and pointed out areas where uncertainty remains.

REFERENCES

1. L. H. Jenks, J. D. Huppler, N. R. Morrow and R. A. Salathiel, Can. Pet. Technol. October–December:172–180 (1968).
2. G. R. Gray and H. C. H. Darley, Composition and Properties of Oil Well Drilling Fluids, Gulf Publishing Company, 1986.
3. Guide to Drilling, Completion and Workover Fluids, World Oil, May 1986, pp. 37–88.
4. J. E. Book, C. C. Mattax and M. O. Denekas, Pet. Trans. AIME 213:155–160 (1958).
5. E. Amott, Pet. Trans. AIME 216:156–162 (1959).
6. D. C. Thomas, H. Hsing and D. E. Menzie, Evaluation of Core Damage Caused by Oil-Based Drilling and Coring Fluids, SPE Paper 13097 presented at the 59th Annual Technical Conference and Exhibition, Houston, Tex., September 16–19, 1984.
7. L. Cuiec, Effect of Drilling Fluids on Rock Surface Properties, SPE Formation Evaluation 4, March 1989, pp. 38–44.
8. J. Yan, J. L. Menezes, and M. M. Sharma, Wettability Alteration Due to Interactions With Oil-Based Muds and Mud Components, SPE Paper 18162 presented at the 63rd Annual Technical Conference and Exhibition, Houston, Tex., October 2–5, 1988.
9. J. Yan and M. M. Sharma, J. Pet. Sci. Eng., in press.
10. M. M. Sharma and R. W. Wunderlich, J. Pet. Sci. Eng. 1: 127–143 (1987).
11. J. J. Rathmell, P. H. Braun and T. K. Perkins, J. Pet. Technol. February:175–185 (1973).

12. W. G. Anderson, J. Pet. Technol. October:1125–1144 (1986).
13. G. J. Hirasaki, Wettability: Fundamentals and Surface Forces, SPE/DOE Paper 17367 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Okla., April 17–20, 1988.
14. N. E. Burke, R. D. Hobbs, and S. F. Kashou, Measurement and Modeling of Asphaltene Precipitation from Live Reservoir Fluid Systems, SPE Paper 18273 presented at the 63rd Annual Technical Conference and Exhibition, Houston, Tex., October 2–5, 1988.
15. J. H. Hansen, A. Fredenslund, K. S. Pedersen and H. P. Ronningsen, AICHE J. 34:1937–1942 (1988).
16. S. W. Yeh, Chevron Oil Field Research Company, personal communication. La Habra, CA 1989.
17. J. B. Auman, A Laboratory Evaluation of Core Preservation Materials, SPE Formation Evaluation 4, March 1989, pp. 53–55.
18. P. K. Hunt and S. L. Cobb, Core Preservation with a Laminated Heat-Sealed Package, SPE Formation Evaluation 3, December 1988, pp. 691–695.
19. D. B. Lerner, Chevron Oil Field Research Company, personal communication. La Habra, CA 1988.
20. P. L. Gant and W. G. Anderson, Core Cleaning for the Restoration of Native Wettability, SPE Paper 14875 presented at the Rocky Mountain Regional Meeting of the Society of Petroleum Engineers, Billings, Mont., May 19–21, 1986.
21. B. F. Swanson, J. Pet. Technol. August:1459–1464 (1980).
22. F. G. McCaffery, J. Can. Pet. Technol. July–September:26–32 (1972).
23. F. Gm McCaffery, R. W. Wunderlich, and R. P. Cartwright, Laboratory and Simulation Studies of Oil Displacement Behavior Due to Bottomwater Drive, SPE Paper 17959 presented at the Middle East Oil Technical Conference and Exhibition, Manama, Bahrain, March 11–14, 1989.
24. D. J. Wendel, W. G. Anderson, and J. D. Meyers, Restored State Core Analysis for the Hutton Reservoir, SPE Formation Evaluation, December 1987, pp. 509–517.
25. F. H. L. Wang, Effect of Wettability Alteration on Water/Oil Relative Permeability, Dispersion, and Flowable Saturation in Porous Media, SPE Paper 15019 presented at the Permian Basin Oil And Gas Recovery Conference of the Society of Petroleum Engineers, Midland, Tex., March 13–14, 1986.

9

Evaluation of Reservoir Wettability and Its Effect on Oil Recovery

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I. INTRODUCTION

To recover oil contained in petroleum reservoirs, waterflooding, sometimes with "improved" water, is widely used. Understanding the phenomena occurring during waterflooding of a porous medium containing reservoir fluids (brine and crude oil) is thus extremely important. Research has long since shown that oil recovery during waterflooding depends on numerous parameters, among which are pore geometry, fluid distribution, saturation, saturation history, and oil/water viscosity ratio [1]. This is why it is always strongly recommended that laboratory experiments of oil displacement by water be performed using the reservoir rock and reservoir fluids, while