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INVESTIGATION OF DISCREPANCIES IN LABORATORY MEASUREMENTS OF LIQUID PERMEABILITY

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Abstract

We have observed increasing reports of discrepancies in laboratory measurements of liquid permeabilities. Possible explanations include rock-fluid interactions, viscous coupling, poor experimentation, and inadequate test procedures.

Our initial work focuses on the influences of experimental techniques and fluid properties on permeability measurements. We found that single liquid phase conditions are often not present within the core samples during flow-through cleaning by miscible solvents. Trace amounts of hydrocarbon contamination in the solvents increases the two phase region of the phase diagram and two phase flow leads to inadequate cleaning.

Understanding the gas saturation and solubility behavior of the fluids used in miscible cleaning and liquid saturating processes is critical in developing laboratory liquid permeability systems. For example, our data on glass micro-models clearly showed the development of a gas saturation when brine displaces methanol. This gas saturation is due to the difference in gas solubility between methanol and brine.

Reliance on visual methods and/or specific flush volume criteria for determining solvent cleaning effectiveness are not adequate. Clear, single phase effluent does not signify pure component flow. Sweep efficiency and gravity effects can cause a miscible solvent mixture to be produced for extended periods.

I. Introduction

Prior to performing laboratory fluid flow measurements, the routine industry practice is to clean the core samples. The selection of the cleaning procedures is based on the possible contaminants that have entered the samples during coring and sampling, and the types of hydrocarbon and brine within the rock. Common methods employed in the core cleaning

process are distillation/extraction, centrifuge flushing, gas driven solvent extraction and/or flow-through solvent flushing. The next step in conventional core preparation is sample drying. Common drying methods used are heat and vacuum drying, humidity controlled drying, forced air drying, and critical point drying. The method selected is normally based on the clay content of the sample and efforts to eliminate or minimize any alteration or damage to the clays.[1]

However, many recent studies have raised questions about sample damage and inadequate cleaning during these initial sample preparation procedures. Three areas of concern are clay alteration caused during heating and drying sequences, inadequate solvent sweeps, and wettability changes that occur during the cleaning process. Many modifications are being made to the routine procedures that have been the industry standard for many years.[2-4] A current approach is to miscibly clean samples and perform fluid permeability measurements prior to using a drying process. Since this eliminates a discrete solvent removal process (drying), the importance of solvent selection becomes crucial. In addition to cleaning effectiveness, miscibility and compatibility between cleaning solvents and final saturating fluids must be considered.

II. Fluid Miscibility Considerations

Accepted procedures for flow-through cleaning are derived from the premise that single phase displacement by miscible fluids will completely replace one fluid by another. The standard technique employs a solvent such as toluene for cleaning hydrocarbons and methanol for removing brine, water, and salt precipitates.[1] It is usually assumed that the complete miscibility of toluene and methanol allows for transition from one solvent to the other without passing through a two phase region where separation may cause incomplete cleaning. However, when hydrocarbon and/or brine contaminants are still present in the system, the magnitude and the shape of the phase envelope is not the same.

Figure 1 shows a 3% KCl brine, toluene, and methanol diagram. Results indicate that it is essentially identical to published data for pure water, toluene, and methanol at 25°C.[5] Figure 2 is the corresponding ternary phase diagram when the toluene is contaminated by 2% mineral oil. It is apparent from this figure that a small amount of hydrocarbon contamination greatly increases the possibility for two phase flow.

Caution should be taken in assuming that a single phase is always present in a core sample that is near completion of the cleaning cycle. If fluid separation occurs during the final stages of the miscible cleaning cycle, the residual fluid may not be mobile and therefore, undetectable. Permeability measured on a core in this state is incorrect because the assumption of 100% saturation is erroneous.
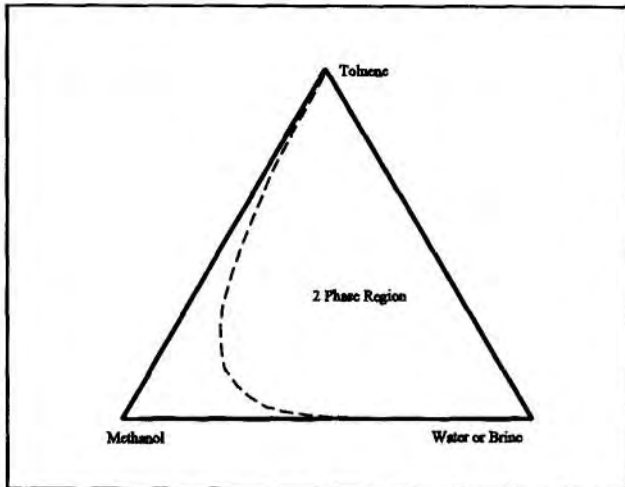
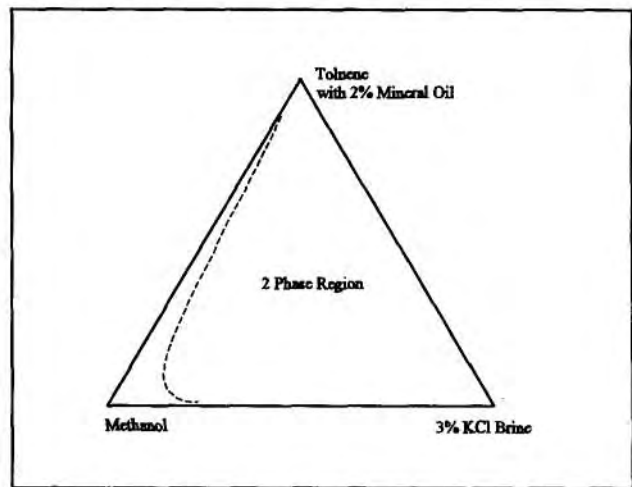**Figure 1.** 3 Component Phase Diagram

Figure 2. Phase Diagram with 2% Hydrocarbon Contamination.

Next we conducted flow experiments to verify interpretations based on the phase diagram work. These experiments were designed to establish the efficiency of miscible flow-through cleaning. We used gas chromatography (GC) to analyze effluent fluids during solvent flushes on a Berea sandstone core containing 3% KCl brine and mineral oil. Figure 3 is a plot of the GC analysis during a 3 pore volume (PV) toluene flush. Results indicate that hydrocarbon expulsion from a sample is a gradual process that requires large amounts of solvent. GC analysis for the subsequent 3 PV toluene flush, Figure 4, after a 3 PV methanol flush, verified that single fluid flow is still not achieved.
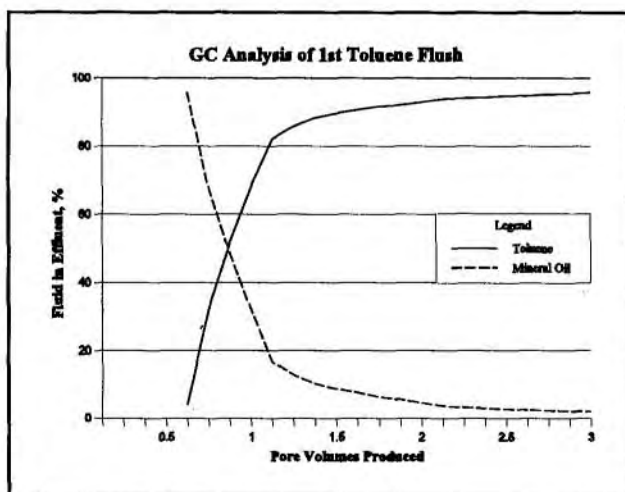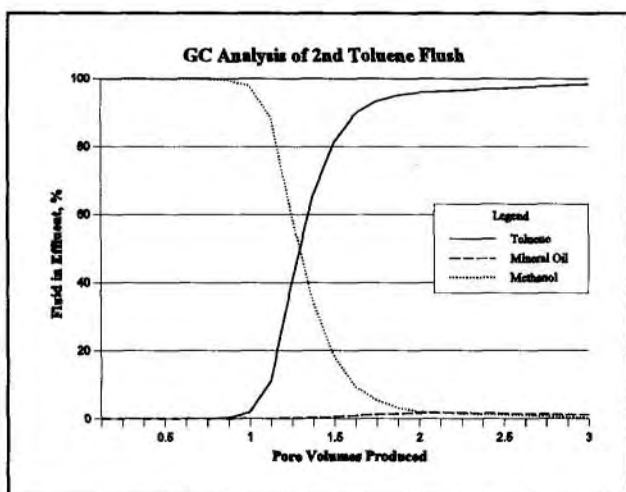

Figure 3. Initial Toluene Flush

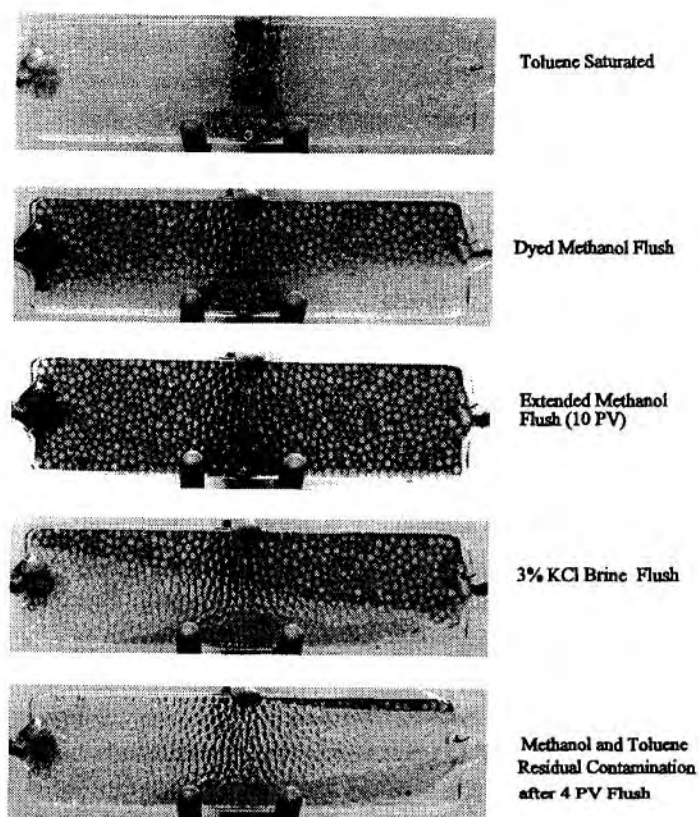**Figure 4.** 2nd Toluene Flush

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Figure 5. Toluene and dyed methanol flushes followed by KCl brine saturation.

We constructed glass micro-models to further investigate miscibility effects. One bead pack model consisted of a single layer of 3mm glass beads packed in a 15 x 3.5 x 4mm glass container. Figure 5 is a series of photographs depicting final solvent and brine flushes of the bead pack. The top photograph shows the toluene saturated sample. We then flushed methanol (dyed blue) through the pack to replace the toluene. Photo No.2 shows the sweep pattern at breakthrough. The observed gravity segregation may or may not occur in core samples, depending on sample permeability, porosity, homogeneity, etc. However, the least swept zone (lower right corner) of the bead pack can be compared to a less permeable zone in a heterogeneous core where flow would be limited. Photo No.3 shows the pack after an extended (10 PV) methanol flush. When 3% KCl brine (clear) is then pumped into the model, two phase separation is clearly visible in the area where methanol flushing of the toluene is not complete. The areas of two phase separation have been enhanced in photos 4 and 5 because reproductions of the originals did not clearly show results. Since the residual contamination has both a cloudy and blue appearance, it suggests both toluene and methanol are present. It is evident that the measured K_w on this assumed single phase, brine saturated sample is not correct. Permeability results obtained from this sample would be low because the calculated absolute K_w would actually be a K_w

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at an unknown S_{or}. We emphasize that the contamination observed here developed in a clean environment using clean fluids. No additional hydrocarbon contamination was needed to trigger two phase separation of the miscible fluids. Further studies in 1 inch internal diameter, 1 mm bead packs behaved similarly and confirmed that miscibility effects must be considered during solvent flow-through cleaning.

III. Effects of Dissolved Gas

The elimination of gas from the fluid stream is important for several reasons. Primarily, the absence of gas from the pore fluid is an indication that complete sample saturation is achieved. Secondarily, elimination of free gas aids experimental measurements during fluid flow tests. Bubbles in the effluent stream can hamper both weight and/or volume measurement of fluids expelled, cause increased pressure fluctuations (noise band) in backpressure regulators, and in some cases, cause degradation in pump performance (cavitation effects).

Various methods specifically directed at batch degassing brine are currently utilized within our industry. The most common methods consist of vacuum techniques, heating, ultrasonic agitation, and helium purging. However, most of these methods are impractical for miscible cleaning because of the volatility of the common solvents used. Therefore, currently adopted miscible flow-through cleaning procedures do not emphasize the need for insuring that all fluids used in the cleaning and saturating process are degassed. The importance of degassing carrier fluids in High Performance Liquid Chromatography (HPLC) applications is understood and well documented.[6] Literature on medical applications like Reversed Phase Liquid Chromatography (RPLC) also routinely caution about bubble formation during mobile phase mixing.[7] Shirota, et al., (1991) presented evidence that batch degassing, though effective, does not maintain a high level of degassed fluid very long. Their results show that within 3 hours after re-exposure to air, gas had redissolved in degassed water to within 75% of its original saturated state and that the water in nearly resaturated within 12 hours.[6] The resaturation rate, of course, will vary with system dimensions. However, total flow intervals per fluid, in our systems, are easily on the order of hours long. Therefore, if batch degassing is not performed frequently, gas saturations of the injected fluids will revert to saturated levels.

Another reason for maintaining all fluids in a degassed state can be explained by examining solubility values of gas for the common fluids used in miscible cleaning. As an example, the solubility of oxygen in 100% methanol is 25.5 vol. % (P=760mm, T=20°C) and in water is 3%. Solubility values gleaned from the literature also show that there is a substantial decrease in oxygen solubility as a function of alcohol concentration in water.[5] Therefore, during a miscible displacement of methanol by a brine, free gas will evolve along the mixing front if degassed fluids are not used.

We used the glass micro-models to visually verify gas evolution during miscible fluid mixing and conducted permeability measurements on a Berea sandstone core loaded in a Hassler Cell system to quantify the effects. The sample was saturated with degassed 3% KCl brine using a backpressure of 200 psi. Figure 6 shows the results of the permeability test sequence after the KCl brine saturation was completed and the backpressure on the pore fluid system was removed. It illustrates that the use of degassed fluids generate more consistent data and that the use of non-degassed fluids or fluids that have resaturated, will cause a dramatic change in measured K_w. Note that since methanol has a higher gas solubility than water, no change in permeability occurs during the fluid displacement of brine by non-degassed methanol, test sequence 4. The major permeability change occurs when the gas saturated methanol evolves gas during dilution in the final brine flush.
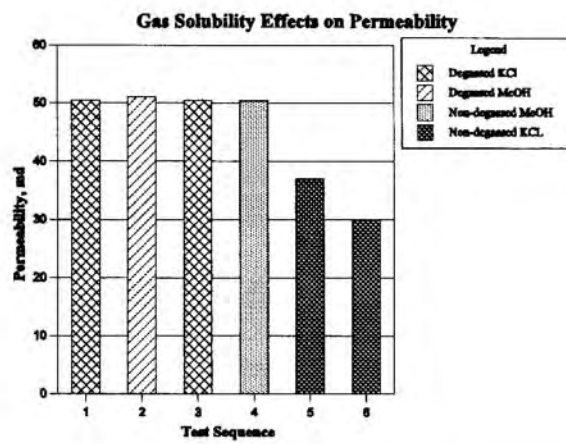

Figure 6. Permeability measurements comparing non-degassed to degassed fluids.

An active, in-line degasser like those employed in HPLC systems, when incorporated into the pore fluid system, eliminates most of the problems associated with gas evolution during cleaning, saturating, and testing. However, even with the incorporation of an active degasser, it is not recommended that miscible cleaning, fluid saturating, and permeability testing be performed without backpressure. The variety and amounts of fluids delivered during all of these processes are substantial and although the presence of gas in these fluids has been greatly reduced, it has not been eliminated. Since gas solubility increases with pressure and gas volume is inversely proportional to the pressure applied, gas effects can be kept minimal if elevated pore pressures are used.

IV. Sweep Efficiency of Miscible Fluids

Crane et al (1963), give the following equation for the effect of gravity on the displacement efficiency for two miscible fluids having the same viscosity, but unequal

densities (e.g. toluene and methanol):[8]

$$\frac{n}{(n-1)^2} = \frac{\phi V \mu}{Kg} \frac{L}{\Delta \rho} \frac{L}{H} = R_{v/g}$$

They defined $R_{v/g}$ as the ratio of the viscous gradient to the gravity gradient and n as the number of pore volumes that must be injected to displace all of the original fluid. They also state that only for $R_{v/g} < 10$ (large gravity forces) has the density difference a significant effect.
Given that:

$$\phi V = \frac{Q}{A} \qquad \text{and from Darcy's equation:} \qquad \Delta P = \frac{Q \mu L}{KA}$$

the equation derived by Crane et al, expressed in laboratory units, can simplified to:

$$\frac{n}{(n-1)^2} = \frac{1.72 x 10^4}{A(cm^2)} \frac{Q(cm^3/min)\ \mu(cp)\ L(cm)}{K(md)\ \Delta \rho(gm/cm^3)\ H(cm)} \qquad \text{or} \qquad \frac{n}{(n-1)^2} = \frac{70.3\ \Delta P(psi)}{\Delta \rho(gm/cm^3)\ H(cm)}$$

The relationships state that if the permeability of a sample is known, $R_{v/g}$ can be calculated for any given flow rate, and when the permeability of a sample is unknown, $R_{v/g}$ and n can still be calculated by measuring the steady state ΔP established during a constant flow rate flush. Application of these equations to laboratory samples indicate that in all but the most extreme cases of permeability, flow rate or sample dimensions, $R_{v/g}$ is well above 10 and n
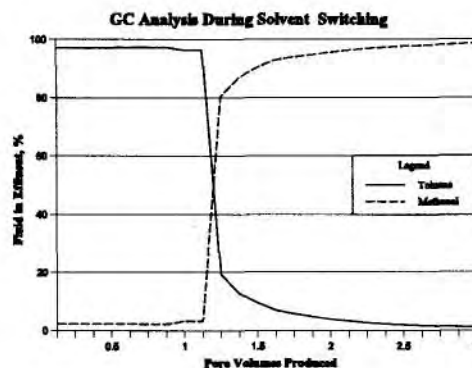

Figure 7. Typical GC Analysis during miscible solvent cleaning.

ranges between 1.0 and 2.0. However, it is routinely observed through GC analysis, Figure 7, that traces of displaced solvent are present in the displacing fluid long after 1-2

pore volumes has been flushed through samples. Possible causes are sample heterogeneity and end effects caused by laboratory system hardware.

The simplest solution for improving sweep efficiency and decreasing gravity effects is a vertical sample orientation during cleaning. Blackwell, et al (1959) defined the critical rate below which gravity segregation will prevent fingering.[9]

The relationship is given by:
$$(\frac{q}{A})_{critical} = \frac{K \Delta \rho g}{\Delta \mu} \sin \alpha$$

or converted to laboratory units:
$$(\frac{q}{A})_{critical}(cm/min) = \frac{5.8 x 10^{-5}\ K(md)\ \Delta \rho (gm/cm^3)}{\Delta \mu (cp)} \sin \alpha$$

For a 1 Darcy sample having a 1 inch diameter, the critical flow rate for methanol displacing toluene is 2.9 cc/min. For a 500 md sample, the critical value is 1.47 cc/min. and for a 100 md sample, the critical value is 0.3 cc/min.

Glass micro-model experiments were again performed using a toluene, methanol, and KCl brine flush sequence on a vertically oriented bead pack. We found thorough cleaning by the flushes as long as we were below gravity stable flow conditions, Figure 8.
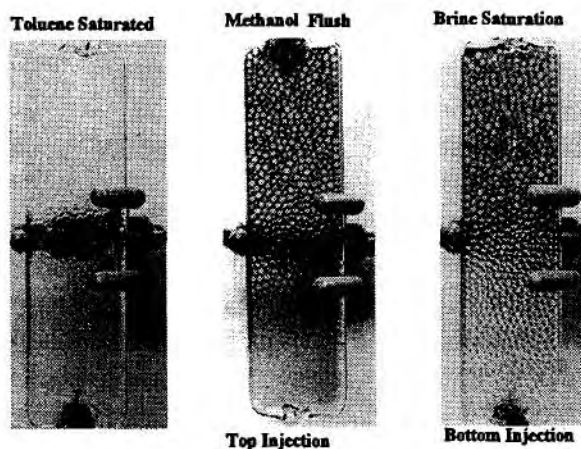

Figure 8. Miscible cleaning using vertical orientation and gravity stable flow.

However, in order to maintain gravity stable flow, the bead pack had to rotated 180° between the methanol (injected from top) and brine floods (injected from bottom). This step in the cleaning process was selected over reversal of fluid flow in order to maintain a consistent flush direction throughout the flow sequences. If a miscible cleaning and

saturating system does not have either capability, then gravity stable flow cannot be maintained during all flushes. Another toluene, methanol, and KCl brine flush sequence on a bead pack was conducted with all of the fluid injection originating from the bottom of the model, Figure 9.
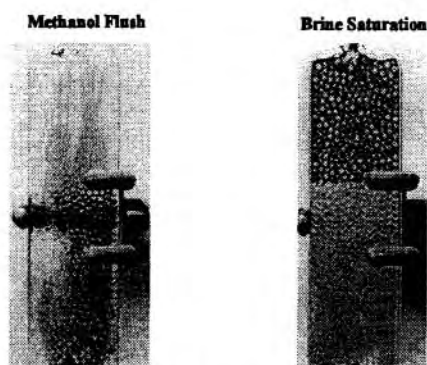

Figure 9. Miscible cleaning in vertical orientation but unstable methanol flush.

It showed extreme fingering as the less dense, dyed methanol was flushed through the toluene saturated pack. Then after a 5 PV methanol flush, the model looked completely methanol saturated. However, a KCl brine flush showed extreme and widely distributed contamination by phase separation of toluene and methanol. Again, because of difficulties in reproducing the original photos, the methanol fingering and the two phase region of the flushes have been enhanced for clarity. This experiment demonstrated that vertical orientation alone, does not increase miscible solvent efficiency. In fact, if care is not taken, this mounting scheme appears to be less effective.

VI. Conclusions and Recommendations

1. Reliance on visual methods and/or specific flush volume criteria for determining solvent cleaning effectiveness are not adequate. Clear, single phase effluent does not signify pure component flow. Sweep efficiency and gravity effects can cause a miscible solvent mixture to be produced for extended periods. If care is not taken, phase separation can occur and cause erroneous permeability measurements.

2. Laboratory liquid permeability systems should always include active on-line degassing capabilities and backpressure regulators. Miscible cleaning and fluid saturation systems should also include these components.

3. The capability for gravity stable fluid flushing will increase miscible cleaning and fluid saturating effectiveness.

VII. Acknowledgements

VIII. Nomenclature

μ =   fluid viscosity of displacing fluid
K =   permeability
K_w =   water permeability (brine), md
S_{or} =   Residual oil saturation, %
g =   acceleration of gravity
$\Delta\rho$ =   density difference
H =   height (or diameter) of model
n =   number of pore volumes injected to displace all of original fluid
ϕ =   porosity
V =   average fluid particle velocity
L =   length of model
Q =   flow rate
A =   cross sectional area
α =   dip angle
$\Delta\mu$ =   viscosity difference
q =   critical flow rate
$R_{v/g}$ =   ratio of viscous gradient to gravity gradient

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