SOME PRACTICAL LESSONS LEARNED
DURING 30 YEARS IN THE SCAL LAB

E. M. (Ted) Braun, consultant

ABSTRACT

This paper discusses several experimental problems and test-planning methods from the author's 30+ year career in core analysis. By promoting awareness of these items, it is hoped that others will avoid unnecessary artifacts and delays in their own lab work.

While the items discussed below are detailed and specific, the lessons learned can be summarized in general terms:
- In experimental work, it is important to consider the behavior of the laboratory hardware and fluids in addition to that of the rock samples being tested.
- When unexpected tests results are encountered, there is long-term value in investigating the causes and making the necessary corrections.
- There is long-term value in communicating experimental failures within a research group and documenting them for future reference. Co-workers may have encountered such failures in the past and be able to suggest solutions.
- The chances of conducting a successful experiment can be increased by calculating the expected results before actually performing lab work.

INTRODUCTION

Special core analysis measurements such as capillary pressure and relative permeability can be experimentally demanding, particularly when conducted at reservoir conditions. Test results can be influenced by a multitude of factors. Some are familiar to most core analysts, such as fluid leaks and variations in temperature and pressure. Less common factors, such as those discussed here, however, can be challenging to identify and correct.

Many of the complicating factors in core analysis involve properties of the materials used in the experiments. These properties are often well known, being tabulated in handbooks and other references, but are not considered when an experimentalist's attention is focused primarily on rock properties.

Potentially flawed experiments can be recognized before a test is actually conducted in the laboratory. Estimates of rock and fluid properties can be used to calculate the basic data expected from an experiment, such as flow rates, pressure drops, and produced fluid volumes. If any of these fall outside the range that can be measured in the experiment, the test design can be changed before the lab tests are actually conducted. In most cases, approximate hand calculations or simple spreadsheets are adequate.

GASES DIFFUSE THROUGH RUBBER AND PLASTICS

Diffusion of small molecules through polymers is a well known phenomenon [1], and forms the basis for a number of industrial processes. In core analysis, however, it is often an unanticipated complication that seems to recur in new and unexpected places, even when steps are taken to avoid it. Three examples from the author's experience are described below:

Example 1: Relative Permeability Test With Live Oil

The author's first encounter with gas diffusion was during a long-term relative permeability test using live oil. Mineral oil was used on the outside of a rubber sleeve, to apply confining pressure to a core. After a period of time, the confining pressure rose from 7500 psi to 8000 psi and continued to climb. A fluid leak was ruled out, since there was no higher-pressure fluid in the apparatus that could be leaking into the coreholder. After eliminating other possibilities, the most likely cause was suspected to be solution gas diffusing from the live oil in the core through the rubber sleeve into the confining fluid, as shown in Figure 1. Although gas was moving against a pressure gradient, it was diffusing from an area of high concentration to one of low concentration, so it didn't violate any laws of thermodynamics. This cause was confirmed when the coreholder was depressured, and the foamy confining fluid was observed. The solution was to use tin foil as a wrap around the core. This has proven to be an effective diffusion barrier in many tests with live oil.
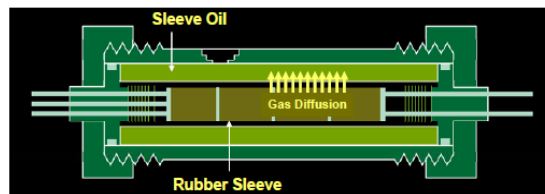

Figure 1. Schematic depiction of gas diffusion from live oil in pore space into sleeve oil used to apply overburden pressure.

Example 2: Use Of Nitrogen As A Confining Fluid

A second encounter with gas diffusion was while making short-term measurements of brine permeability, in order to choose core samples for later tests. It was typically a simple process to load a core into a coreholder, apply confining pressure with nitrogen, pump brine, and measure the pressure drop. In one case, however, the coreholder was kept pressurized overnight. The permeability was much lower the next morning, but recovered after flowing brine against back pressure. Overnight was long enough for nitrogen to diffuse from the confining space into the pore space, form a gas saturation in the core and decrease the effective brine permeability.

Example 3: Use Of Teflon Gas Sampling Bags

A third case of gas diffusion was a lab test that involved collecting solution gas in a flexible gas bag for compositional analysis. Even though care was taken to exclude air from the sample, the analysis showed a high concentration of nitrogen/oxygen (which were not separated in the chromatographic method being used.) The problem was solved by substituting an aluminum-laminate gas bag for the single-layer Teflon bag that had allowed air to diffuse into the sample.

TIN DEGRADES WHEN STORED FOR EXTENDED TIMES AT LOW TEMPERATURES

In our laboratory, it became common practice to stabilize unconsolidated core plugs by applying screens at the plug ends and a wrap of Teflon tape and tin foil around the circumference. When external stress is applied briefly, the tin conforms well to the plug and the assembly can be handled as if it was consolidated rock. In some cases, unconsolidated core plugs were also stored in a freezer, where the ice in the pore space prevents grain rearrangement (as long as the water saturation is not too high) and the low temperature greatly reduces evaporation of oil and water.

In cases where both tin and freezing were used, millimeter-size holes were sometimes discovered in the tin after long storage periods, as shown in Figure 2. This was puzzling because neither corrosion nor rough handling seemed likely.

Finally, a co-worker suggested that the case was "tin pest", a change in the crystal structure from the β form (metallic white tin) to the α form (grey tin, a powder). In its pure form, white tin is only stable above 13.2°C, and slowly converts to grey tin at lower temperatures. [2]

Figure 2. Tin-wrapped unconsolidated core plug showing holes from "tin pest" after long-term cold storage.

The change in crystal structure is shown in Figure 3 and a dramatic time-lapse video of this phenomenon is available on the internet. [3]

The phenomenon has long been recognized by chemists and historians. It has been given as the reason for deterioration of objects such as organ pipes in European churches, fuel cans in Antarctica, and the buttons on the uniforms of Napoleon's soldiers during their 1812 invasion of Russia. [4] But, to our knowledge, this information had not become known in the field of core analysis.

β (white) tin
body-centered tetragonal structure
density 7.29 g/cc

α (grey) tin
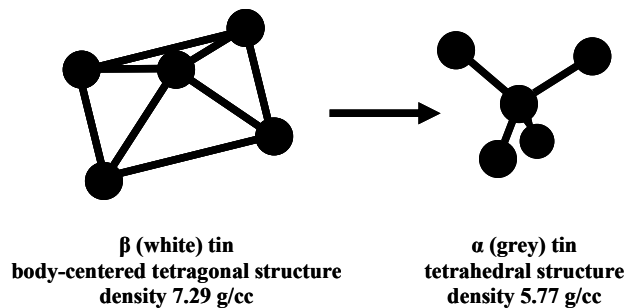**tetrahedral structure**
density 5.77 g/cc

Figure 3. Change in crystal structure of tin below 13.2°C.

The solution has been to avoid the use of tin at low temperature. Nickel foil is a good substitute, or tin-wrapped plugs may be stored at room temperature.

SOME OIL-WATER SEPARATORS REQUIRE UNIFORM FLUID DENSITIES

Anomalous data has been obtained from laboratory oil-water separators that remotely sense fluid interfaces. In one case, an unsteady-state relative permeability test appeared to temporarily indicate a negative rate of oil production, as shown qualitatively in Figure 4. The cause was identified as a difference in density between the incoming brine and the brine originally present in the separator, as shown in Figure 5. Since the separator sensed the difference in gravity head between two fluid columns, it was affected by changes in brine density in addition to changes in oil volume. [5]
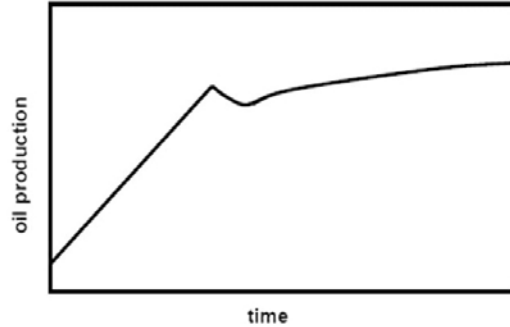

Figure 4. Oil production curve from unsteady-state waterflood conducted with non-uniform brine density.
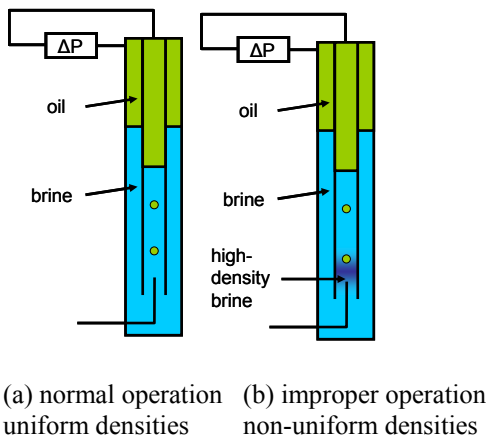

(a) normal operation   (b) improper operation
uniform densities   non-uniform densities

Figure 5. Normal and improper operation of gravity-head separator.

(a) normal operation   (b) improper operation
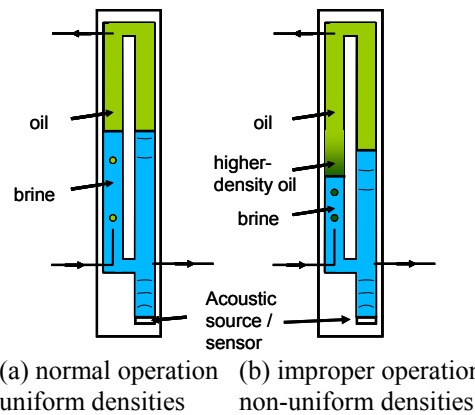uniform densities   non-uniform densities

Figure 6. Normal and improper operation of acoustically-monitored separator.

Separators of the acoustically-monitored two-bore type shown in Figure 6 are also affected by variable fluid densities. They rely on the interface level in the static measurement bore being the same as that in the dynamic production bore. This is a reliable method when the oil and water each have uniform density. However, varying densities can cause the two interface levels to be different, even when the system is in hydrostatic equilibrium.

The solution has been to avoid the use of such separators in lab tests that investigate compositional phenomena such as salinity sensitivity and injection of non-equilibrium gases. Such tests are generally conducted, not with recirculation, but with once-through flow followed by collection and analysis of produced fluids.

CHLORINATED HYDROCARBONS CAN REACT WITH WATER AT ELEVATED TEMPERATURE TO FORM HYDROCHLORIC ACID

This chemical reaction was first observed when core samples from a carbonate reservoir were subjected to Dean Stark extraction using 1,1,1-trichloroethane, without first removing the water from the pore space. When removed from the extractor, the cores were pitted where the condensed solvent had dripped on the core surfaces. Although no chemical analysis was performed in this case, it was suspected that the samples had been etched by hydrochloric acid that had formed from the solvent and water. Further evidence was obtained from the literature. [6] Similar extractions with water-free samples did not show this pitting, suggesting that water was a necessary chemical reactant.

More definite evidence of this reaction was obtained in a later study. Hydrocarbon residue was being removed from a core by flow-through cleaning with a chloroform-methanol mixture (azeotrope) at reservoir temperture, approximately 200°F. The effluent was initially black in color, as expected, but became green as the cleaning progressed. Chemical analysis showed that the effluent was highly acidic and contained iron and nickel. The conclusion was that hydrochloric acid had formed and reacted with stainless steel tubing. Although water had been removed from the core, the methanol used to prepare the azeotrope had probably absorbed water from the atmosphere. In subsequent work, this problem has been prevented by either:

- preparing the azeotrope using an unopened bottle of methanol, which had not had the opportunity to absorb water
- using chloroform and other chlorinated solvents at room temperature

In addition, the use of stainless steel tubing has been discontinued, in favor of Hastelloy C-276, which is more resistant to corrosion and stress-corrosion cracking.

INK FROM FELT-TIP PENS IS REMOVED BY SOLVENTS

A common error by entry-level lab workers is to use a felt-tip marker to label core plugs. This error often goes unnoticed until the plugs are subjected to Dean Stark extraction or other solvent treatment, when the markings disappear. In one case in our own laboratory, we were fortunate in being able to use plug dimensions and geologic rock type to re-identify the plugs. More appropriate labeling would have used India Ink or pencil, both of which are unaffected by most solvents. Another approach is to place each sample in an extraction thimble labeled with India Ink or pencil.

HEAT-TRACED FLOW LINES DO NOT HAVE UNIFORM TEMPERATURES

When relative permeability tests are conducted at reservoir conditions using closed-loop recirculation, it is rare to encounter experimental problems related to fluid behavior. An exception is tests conducted in the apparatus shown in Figure 7, in which fluids are circulated between a constant-temperature oven and a heated coreholder located in an X-ray scanner, with the connecting tubing wrapped

Figure 7. Recirculating relative permeability apparatus with oven and core connected by heat-traced tubing.

with electrical heating tape. [7] In this apparatus, flow blockages have been encountered on several occasions while testing carbonate cores.

The cause of the blockage was identified as precipitation of calcium sulfate in the tubing connecting the oven and the coreholder. Handbook data revealed that calcium sulfate has reverse solubility behavior, i.e. is less soluble at higher temperature. [8] As a result, some brines will form precipitates at "hot spots" in the apparatus. It is nearly impossible to achieve a uniform temperature with heating tape, particularly when the heated components have non-uniform geometry, such as assemblies of tubing, valves, and fittings.

In some cases, tests can be run with brine that is not saturated with calcium sulfate, but this can cause other problems, such as dissolving anhydrite from core samples, or causing concern about flow properties changing with brine composition.

TESTS SHOUD BE REHEARSED USING SIMPLE CALCULATIONS BEFORE BEING CONDUCTED IN THE LABORATORY

This approach allows inappropriate test procedures to be identified and corrected before beginning laboratory work. Methods of rehearsing a test may include:
- Assuming rock properties and calculating the raw data expected from the test
- Calculating the time or fluid volume required to complete the test
- Using a schematic diagram to evaluate a proposed valve opening sequence

In nearly all cases, any required calculations are simple and can be carried out by paper and pencil, or in a simple computer spreadsheet.

Example 1: Measuring Brine Permeability
Measurements of liquid permeability can be slow to equilibrate when using an apparatus with large pumps and transfer vessels such as that shown in Figure 8. The measured pressure drop approaches its equilibrium value exponentially, characterized by a time constant τ, as shown in Figure 9. The measured data can be considered sufficiently accurate after an elapsed time of 3-5 time constants. The time constant can be calculated from the volumes and compressibilities of the upstream fluids and the flow resistance of the core. As shown in Table 1, such a calculation would give a time constant that is acceptable (~2 minutes) for a 1 milliDarcy core, inconvenient (~20 minutes) for a 0.1 milliDarcy core, and impractical (~200 minutes) for a 0.01 milliDarcy core. Major improvements in response time can be achieved by eliminating the transfer vessel and pumping the test fluid directly using a low-volume pump. On the other hand, slower response times would be expected if air is present in the upstream volume.
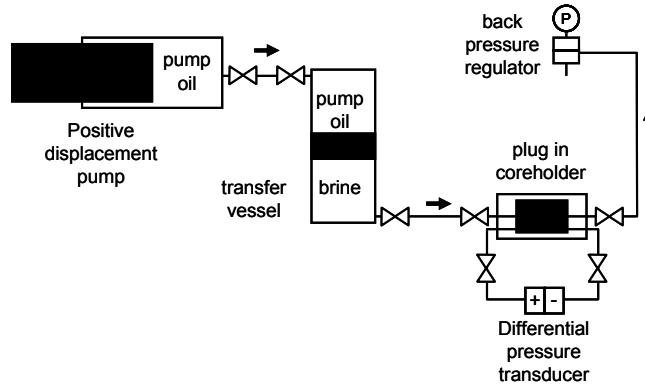

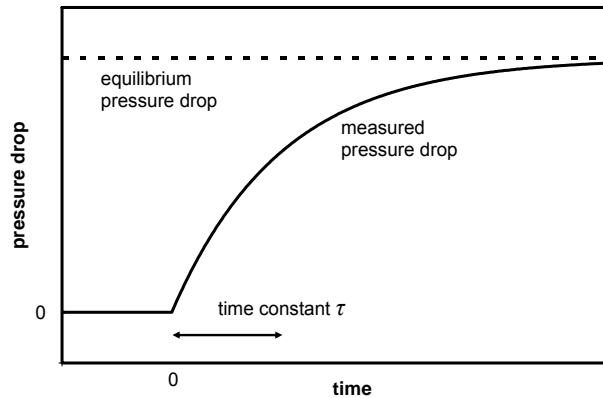Figure 8. Apparatus for measurement of brine permeability.

Figure 9. Exponential approach of measured pressure drop to equilibrium value.

Table 1. Sample calculation of time constant for equilibration of brine permeability measurement.

upstream capacitance (apparatus-dependent)			
V_o	oil in pump	500	cc
	oil in transfer vessel	1000	cc
V_w	brine in transfer vessel	1000	cc
C_o	oil compressibility	1.E-05	psi^{-1}
C_w	brine compressibility	3.E-06	psi^{-1}
$C = C_o V_o + C_w V_w$	upstream capacitance	0.018	cc/psi

Table 1 (cont'd). Sample calculation of time constant for equilibration of brine permeability.

flow resistance (core-dependent)					
k	core permeability	1	0.1	0.01	mD
l	core length	5.08	5.08	5.08	cm
A	core cross-sectional area	11.4	11.4	11.4	cm^2
μ	brine viscosity	1	1	1	cP
$R = \dfrac{\Delta P}{q} = \dfrac{245 \; \mu \; l}{k \; A}$	flow resistance	109.18	1091.8	10918	psi/(cc/min)

time constant (dependent on apparatus and core)				
$\tau = R \; C$	time constant	1.97	19.65	196.52	min

Example 2: Choice Of Fractional Flow In Steady-State Relative Permeability Tests

In an early measurement of relative permeability by the steady-state method, the author arbitrarily selected fractional flow values of 0, 25, 50, 75, and 100%. The result was points on the relative permeability curves that were clustered in a narrow saturation range, as shown schematically in Figure 10. A simple calculation of fractional flow vs. saturation, using estimated relative permeability curves, would have predicted this, regardless of whether the estimated curves were correct for this specific core. It soon became common practice to use more fractional flow

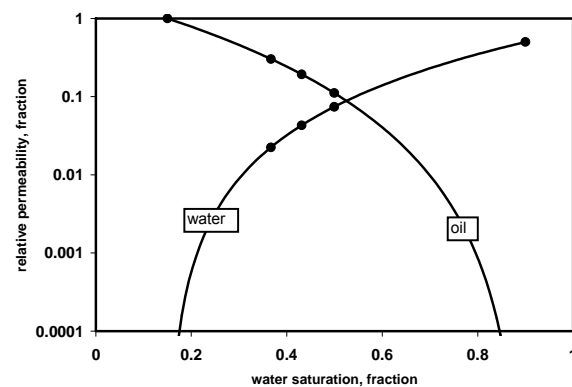
Figure 10. Relative permeability data clustered at intermediate saturations when measured at water fractional flows of 0, 25, 50, 75, and 100%.

values near the extremes and fewer intermediate values, in order to better define the relative permeability curves.

Example 3: Measuring Low Values Of Water Relative Permeability By The Steady-State Method

When measuring water-oil relative permeability, it is desirable to measure one or more data points at low values of water relative permeability, which occur at water saturations only slightly above irreducible. Such data points help define the shape of the k_{rw} curve and aid in fitting equations to the data.

Using the steady-state method, however, measuring such points can be slow because water is injected at very low water fractional flows, limiting the rate of saturation change. Unreasonable test durations can be avoided by estimating equilibration times during planning of the test, and making adjustments if necessary.

The minimum time for equilibration is given by $t = PV/q(\Delta f_w / \Delta S_w)$, where PV is the pore volume of the core, q is the total (oil and water) flow rate, and $\Delta f_w / \Delta S_w$ is the slope between the first two measured points on the fractional flow curve. Determination of this slope is shown in Figure 11 using a small portion of the fractional flow curve. While the actual fractional flow curve is not known before an experiment, it can

Figure 11. Determining minimum equilibration time from slope between first two measured points on the fractional flow curve.

be estimated by assuming relative permeability curves for the oil and water phases. In our experience, even a rough estimate can indicate whether a proposed fractional flow point can be measured in a reasonable time, and can provide an estimate of the k_{rw} value that will be measured.
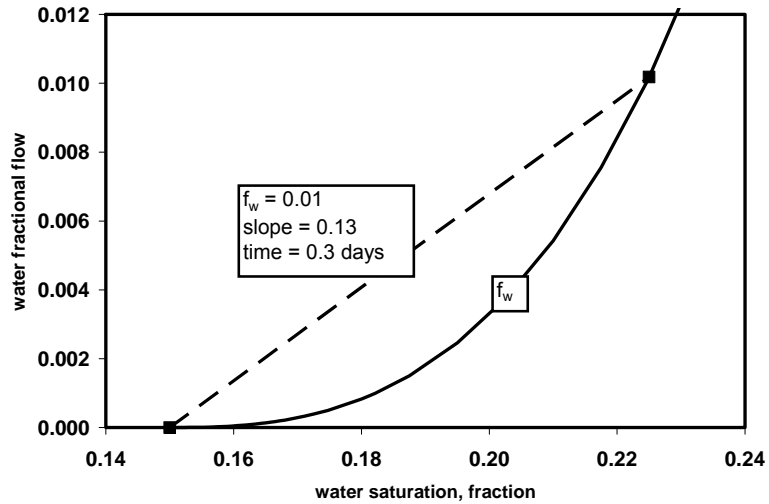
Table 2 and Figure 12 show an example in which minimum equilibration times are judged to be acceptable (under 2 days) if the fractional flow of water is 0.001 or greater, but unacceptable if the fractional flow is 0.0001. In practice, somewhat longer times are needed to ensure that steady-state conditions have been achieved.

Calculations of this type indicate that measurements of very low water relative permeability values are more feasible under the following conditions:
- High permeability cores (therefore high flow rates)
- High viscosity ratio μ_o / μ_w (steeper fractional flow curve near irreducible water saturation)

Table 2. Calculation of minimum equilibration times for proposed fractional flows.

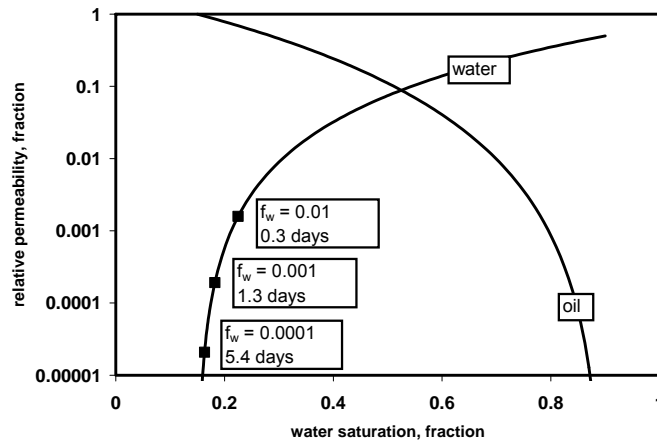| PV	pore volume	60			cm^3
q	flow rate	1			cm^3/min
S_{wi}	initial water saturation	0.15			fraction
f_w	water fractional flow	0.0001	0.001	0.01	fraction
S_w	water saturation at f_w	0.163	0.182	0.225	fraction
slope	$\Delta f_w / \Delta S_w$	0.0077	0.031	0.13	
$t = PV/q(\Delta f_w / \Delta S_w)$	minimum equilibration time	7800	1920	450	minutes
$t = PV/q(\Delta f_w / \Delta S_w)$	minimum equilibration time	5.4	1.3	0.3	days

Figure 12. Example of relative permeability values and minimum equilibration times for proposed experimental fractional flows.

Example 4: Evaluating Potential For Water Evaporation During Gas Flow

In early gas-water relative permeability tests with high permeability core samples, material balances errors were noted. At the end of the tests, the cores contained less water than expected based on the initial water content and the measured production. Simple calculations showed that water evaporation should have been expected, based on the vapor pressure of water and the volume of gas flowing through the core.

To avoid this in the future, it became common to calculate, before the test, the potential for water evaporation, and conduct the experiment in a way that controlled evaporation. Several strategies have been used, depending on the results of the calculations. These are discussed briefly below:

- **Stopping the test after a specified amount of gas throughput:** This generally applies to samples with very high permeabilities, for which high throughput volumes are possible. It may mean, however, stopping a relative permeability test at a water saturation higher than would otherwise be obtained.

- **Humidifying the incoming gas by contacting it with brine:** This happens naturally when the gas is recirculated, as in the method described by Wang et al. [9]. When fluids are not recirculated, humidifying the gas complicates the experiment slightly by requiring additional hardware components. Water evaporation from the core is greatly reduced, but not completely eliminated, since gas becomes undersaturated as it expands due to pressure drop along the core length.

- **Cooling the core to room temperature before injecting gas:** This reduces evaporation by greatly reducing the vapor pressure of the water that is contacted by the gas. It has been used when measuring effective gas permeability after high-temperature centrifuge tests. A disadvantage is that it is a departure from the philosophy of reservoir-conditions testing.

- **Injecting non-humidified gas:** For lower-permeability cores, calculations may show that it is not feasible to inject enough gas to cause significant evaporation. In this case, an acceptable experiment can be run without the complications of humidifying the gas.

CONCLUSIONS

Several experimental problems encountered in special core analysis studies have been described. All were experienced by the author and co-workers over a 30+-year career in special core analysis.

While the items discussed below are detailed and specific, the lessons learned can be summarized in general terms:
- In experimental work, it is important to consider the behavior of the laboratory hardware and fluids in addition to that of the rock samples being tested.
- When unexpected tests results are encountered, there is long-term value in investigating the causes and making the necessary corrections.
- There is long-term value in communicating experimental failures within a research group and documenting them for future reference. Co-workers may have encountered such failures in the past and be able to suggest solutions.
- The chances of conducting a successful experiment can be increased by calculating the expected results before actually performing lab work.

ACKNOWLEDGEMENTS

REFERENCES

1. Crank, J. and Park, G.S., editors, *Diffusion in Polymers*, Academic Press, New York (1968).

2. Lide, D. R., editor, *CRC Handbook of Chemistry and Physics, 84th Edition*, CRC Press, Boca Raton, FL (2003-2004), page 4-32.

3. periodictable.ru: "tin pest, transformation of beta tin into alpha modification (grey tin)", YouTube.com., accessed 19 March 2011
   http://www.youtube.com/watch?v=sXB83Heh3_c>

4. Emsley, J., *Nature's Building Blocks: An A-Z guide to the Elements*, Oxford University Press; Oxford, U.K. (2001), pp 445-450.

5. Hvolboll, V. T., "Method for Accurately Measuring Produced Oil Volumes During Laboratory Waterflood Tests at Reservoir Conditions," *Society of Petroleum Engineers Journal* (August, 1978) 239-241.

6. McKetta, J. R., editor, *Chemical Processing Handbook*, Marcel Dekker, Inc., New York (1993), p. 376.

7. Chen, A. L. and Wood, A. C., "Rate Effects on Water-Oil Relative Permeability," *SCA2001-19, Edinburgh*, Sept. 17-19, 2001.

8. Garverick, L., *Corrosion in the Petrochemical Industry*, ASM International, Materials Park, OH (1994), p 101.

9. Wang, F. H. L., Braun, E. M., Kuzan, J. D., Djabbarah, N. F., Honarpour, M. M., Chiasson, C. G., and Milligan, B. E., "Application of Unique Methodology and Laboratory Capability for Evaluation of Hydrocarbon Recovery Processes," *IPTC Paper 12418, presented at the International Petroleum Technology Conference*, Kuala Lumpur, Malaysia, Dec. 3-5, 2008.