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Use of Vapor Desorption Data to Characterize High Capillary Pressures in a Basin-Centered Gas Accumulation with Ultra-Low Connate Water Saturations

K.E. Newsham, SPE, Anadarko Petroleum Corp., J.A. Rushing, SPE, Anadarko Petroleum Corp., and P.M. Lasswell, OMNI Laboratories, Inc.

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Abstract

This paper presents results of a laboratory study of capillary pressure characteristics of core samples from the Bossier sands in the Mimms Creek Field located in Freestone Co., TX. The Bossier tight gas sand play is believed to be part of a basin-centered gas system (BCGS) in the East Texas Basin. Similar to other BCGSs, the Bossier sands are sometimes characterized by an abnormally high capillary pressure profile associated with an ultra-low connate water saturation distribution. We use a vapor desorption technique to measure capillary pressures as high as 10,000 psi and corresponding to water saturations as low as 1%. We also compare capillary pressures measured with a centrifuge and demonstrate our inability to fully define the pressure-saturation range observed in the Bossier sands using a centrifuge.

Introduction

Tight gas sands constitute a significant percentage of the U.S. natural gas resource base and offer tremendous potential for future reserve growth and production. A recent study by the Gas Technology Institute[1] indicated tight gas sands comprise almost 70% of gas production from all unconventional gas resources and account for 19% of the total gas production from both conventional and unconventional sources in the U.S. The same study[1] estimated total producible tight gas sand resources exceed 600 Tcf, while economically recoverable reserves are 185 Tcf.

Basin-centered gas systems (BCGS) represent an important component of the tight gas sand resource base.[2] A BCGS is generally defined as a regionally pervasive, low-permeability sand accumulation that is gas saturated, is abnormally pressured, and lacks a down dip water contact.[3] Similar to conventional oil and gas systems, BCGSs are often described by complex geological and petrophysical systems as well as heterogeneities at all scales. Unlike conventional reservoirs, however, BCGSs often exhibit unique gas storage and producing characteristics. Moreover, many BCGSs, especially those in deeper basins, are also characterized by very low connate water saturations and the associated high capillary pressures. Consequently, effective exploitation of these resources requires accurate description of key reservoir parameters, particularly capillary pressures, to quantify the vertical water saturation distribution and resource-in-place. Unfortunately, limited capillary pressure data from BCGSs have been published in the petroleum literature.

Previous studies of Bossier sands in the Mimms Creek Field and in deeper parts of the East Texas Basin have suggested that these sands are part of a basin-centered gas system.[4,5] In addition, these previous studies documented the presence of an ultra-low (*i.e.*, sub capillary-equilibrium) water saturation distribution in the Bossier sands.[5] The goal of our current laboratory study, therefore, was to describe the capillary pressures associated with these low saturations.

Numerous techniques have been developed for measuring capillary pressures, including porous plate, centrifuge, and mercury injection. The primary advantage of the porous plate and centrifuge methods is the ability to use reservoir fluids during the pressure measurements; however, limitations on the maximum achievable pressure preclude application in most tight gas sands. High-pressure mercury-injection can reach the necessary pressures, typically 5,000 to 10,000 psi, but the use of non-reservoir fluids to compute capillary pressures accurately at reservoir conditions has been questioned. Accordingly, we used the vapor desorption technique[7-11] to measure capillary pressures, especially at ultra-low water saturations.

We present results from a laboratory study of the Bossier tight gas sand play in the Mimms Creek Field located in Freestone Co., TX. Core samples obtained from the field had permeabilities ranging from 0.0006 to 0.14 md, while effective porosities ranged from 5 to 13 percent. We measured capillary pressure characteristics using both a vapor desorption method and a high-speed centrifuge. Capillary pressures, measured using the vapor desorption technique, exceeded 10,000 psi for water saturations ranging from 1 to 10 percent. Maximum capillary pressures measured from the high-speed centrifuge reached only 1,000 psi for water saturations ranging from 10 to 70 percent. We compare these capillary pressure measurements and illustrate the applicability of the vapor desorption technique for tight gas sands, especially BCGSs.

Regional Geology and Depositional Environment of the Bossier Sands

The Bossier sands (Fig. 1) are part of the Upper Jurassic-age Cotton Valley Group deposited in the East Texas Basin.[11] The Bossier interval, lying immediately beneath the Cotton Valley Sandstones, is a thick, lithologically complex system containing black to gray-black shales interbedded with fine-grained to very fine-grained argillaceous sandstones. The Cotton Valley Group is underlain regionally by the Upper Jurassic Louark Group, which includes other hydrocarbon-bearing formations such as the Smackover Carbonates and Haynesville/Cotton Valley Limestones. Overlying the Cotton Valley Group are the regionally productive Lower Cretaceous Travis Peak and Pettit formations.

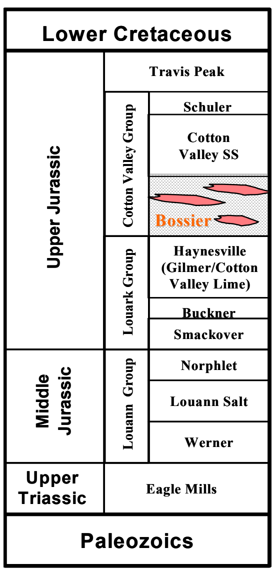


Fig. 1—Stratigraphic column for the Bossier Sands, East Texas Basin.[11]

Bossier sand deposition represents cycles of sand progradation into the basin and onto organic-rich mud, succeeded by marine transgression. Much of the Bossier interval down-dip appears to be time equivalent to the Cotton Valley Sandstones up-dip and represents pro-delta/delta-front material related to Cotton Valley deltaic systems. Bossier sands appear to originate from the north and west and were transported down-slope by slumping, debris flow, and turbidity currents. Significant Bossier sand thickness is located in topographic lows created by a combination of faulting, subsidence, and salt movement within the basin.

The Bossier sands in Mimms Creek Field are comprised of a series of stacked sand-shale packages, illustrated by the type log in Figure 2. In chronological order of deposition, these sand packages are the Bonner/York, Shelley, and Moore sands. Stratigraphic sequences observed from several whole cores indicate the sands were deposited as a prograding sediment wedge complex during a low-stand onto organic shelf mud deposited during a high-stand. At the top of the sand packages, transgressive lag deposits have been observed indicating the onset of a marine transgression during which very little sand was preserved above wave base. The Bossier sands are capped by restricted to open shelfal muds deposited during another highstand.

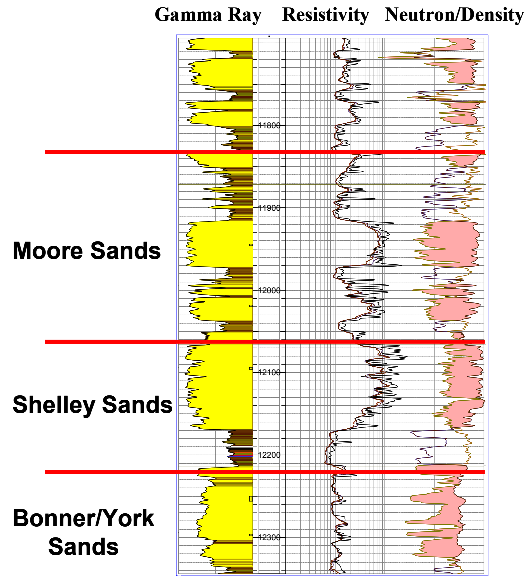


Fig. 2—Type log for the Bossier sand sequence in the Mimms Creek Field, Freestone Co., TX.

Petrophysical Description of Bossier Sands in the Mimms Creek Field

A comprehensive Bossier sand description program, including more than 1,000 ft of whole core obtained from three wells in the Mimms Creek Field, provided the petrophysical data base for our study. Our description included classification of petrophysical rock types,[12,13] which are identified based on similar pore- and grain-scale characteristics. We have also defined several hydraulic rock types[13] representing similar ranges of storage and flow characteristics. Most of the whole core was obtained with an oil-base mud in an effort to quantify the *in-situ* connate water saturation more accurately.

Petrographic Rock Types. Petrographic rock types were identified according to similar constituent mineral distribution, composition and habitat using thin section descriptions, x-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM) imaging. Bossier sand petrographic rock types[13] include clean sandstone, argillaceous/weakly laminated sandstone, dolomitic sandstone, and argillaceous/burrowed siltstone. The Folk[14] classification ranges from sub-arkose to sub-litharentite to lithic wackes. Framework grains contain 84% quartz, 6.5% feldspar, and 9.5% rock fragments.

The intergranular constituents are primarily quartz overgrowths, diagenetic clay in the sands, detrital clay found in sand and silt, dolomite cement, and local pyrite. The clay fraction is dominantly grain-coating chlorite and illite. Texturally, the Bossier sands have a narrow range of grain size, typically from upper very fine to fine. The sands are medium to well sorted, while the silts are typically poorly sorted. Sand grain shape is sub-angular to well rounded. A significant degree of compaction is observed from thin sections in the form of suturing, elongation of grain contacts, and ductile grain deformation.

Similar to most tight gas sands, the Bossier sands have also been modified significantly by diagenesis. The most important forms of diagenesis are mechanical compaction, cementation from quartz overgrowths, grain-coating/pore lining clay development, and grain dissolution. Although less important and prevalent, carbonate cementation has also been observed. Figure 3a is a SEM photograph showing the presence of illite and chlorites and their effect on the rock pore structure, while Figure 3b is a thin section micro-photograph of the same rock illustrating the presence of quartz overgrowths.

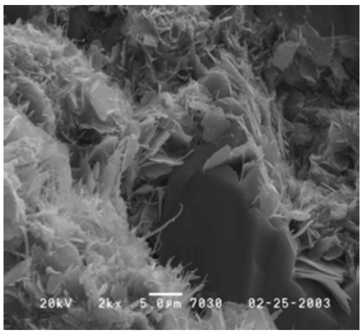


Fig. 3a—SEM micro-photograph showing common clays in the Bossier tight gas sands, Mimms Creek Field.

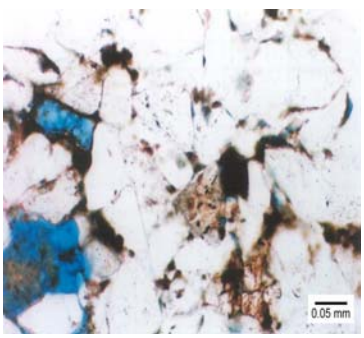


Fig. 3b—Thin section micro-photograph showing quartz overgrowths in the Bossier tight gas sands, Mimms Creek Field.

Hydraulic Rock Types. We have also identified several Bossier sand hydraulic rock types.[13] When described on the basis of the dominant pore throat diameter determined from high-pressure mercury capillary pressure data, we observed distinct groupings of rocks having similar flow and storage properties, *i.e.*, hydraulic rock types. Figure 4 is an example of an incremental mercury intrusion plot used to identify rock types.[13,15-18] The mercury intrusion plot quantifies not only the range but also the dominant pore throat radius.

Figure 5 shows the general region of each rock type in porosity-permeability space. Hydraulic rock types 1, 2A, 2B, and 3A are all considered to be reservoir rock. Because of their low permeability, high initial water saturation and significant degree of vertical heterogeneity, rock types 3B and 4 are non-reservoir rocks and probably act as flow baffles, barriers, and seals. Effective porosity in the Bossier sands in the Mimms Creek Field varies from 1% to 15%, while absolute permeability of reservoir rock ranges from 0.001 to 1 md. Non-reservoir and seal rocks typically have permeability values lower than 0.001 md.

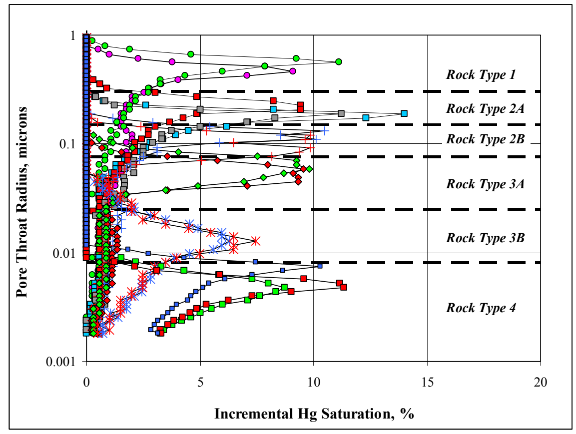


Fig. 4—Incremental mercury intrusion plot used to identify hydraulic rock types for the Bossier sand.

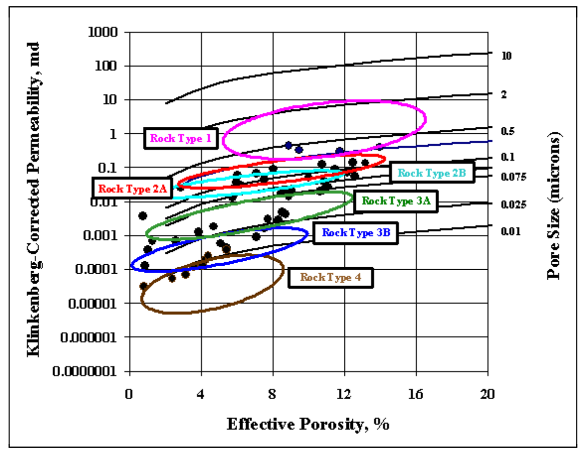


Fig. 5—Range of porosity and permeability for Bossier sand hydraulic rock types.

Water Saturation and Salinity. *In-situ* connate water saturations were measured from several hundred core samples obtained with an oil-base mud program.[5] Water saturation in the reservoir-quality rock ranged from as low as 5% in the most permeable rock to as high as 50% in the lower-quality reservoir rock. Furthermore, water saturations generally exceeded 60% in the non-reservoir rock types. We also verified the core-based vertical distribution of water saturation using both log- and capillary-based calculations.[5]

Salinity of the in-situ connate water was measured using both micro-thermometry fluid inclusion and commutation (*i.e.*, residual salt) analyses. The results suggested the range of salinity in the Bossier sand connate waters is 180,000 to more than 350,000 ppm. We believe these abnormally high salinities and ultra-low water saturations are probably a result of a water vaporization process caused by movement of dry hydrocarbon gas through the system.[5]

On the basis of several previous studies, we have observed an abnormally high capillary pressure profile associated with the ultra-low (*i.e.*, sub capillary-equilibrium) water saturation distribution. Although not common in the petroleum industry, this phenomenon has been observed and documented in basin-centered gas systems.[2,3] In fact, we believe the Bossier sands are part of a basin-centered gas accumulation in the East Texas Basin.[4]

Theoretical Aspects of Capillarity in Porous Media

According to Collins,[19] a wetting fluid or liquid is retained within a porous medium by two types of forces: surface forces hold the liquid as a molecular film completely covering the rock surfaces, and capillary forces hold the liquid as a bulk fluid with curved interfaces separating the liquid and vapor phases. Surface forces include the cohesive attraction of molecules between like substances, interfacial tension between immiscible fluids, adhesion or the attraction of molecules between unlike substances, and surface chemical properties that can lead to ionic bonds. Moreover, the partial pressure of a vapor in equilibrium with the bulk liquid is a function of the curvature of the vapor-liquid interface. We know from the Young-Laplace equation that capillary pressure is also a function of the liquid surface curvature. Finally, since the liquid interface curvature depends on saturation, then it follows that the partial pressure of a vapor is also dependent on the liquid saturation.[19]

Calhoun,[20] Collins,[19] and Melrose,[6] have derived a relationship between capillary pressure and vapor pressure lowering for a pore system containing water in equilibrium with its vapor. Written in terms of partial pressures, the equation is

$$P_c = \ln\left(\frac{p_{v1}}{p_{v2}}\right)\frac{RT}{V_m} \quad \text{.......} \quad (1)$$

where

P_c = capillary pressure, psi
p_{v1} = partial vapor pressure for brine within the pores
p_{v2} = partial vapor pressure for equilibrating salt solution
R = universal gas constant, 8.314 J/Mol K
T = absolute temperature, degrees Kelvin
V_m = molar volume of water

Equation (1) can be rewritten in terms of relative humidity as follows:

$$P_c = -\frac{\ln(RH/100)RT}{V_m} \quad \text{.......} \quad (2)$$

where RH is the relative humidity of the water vapor.

Equations (1) and (2) describe mathematically the effect of changes in vapor pressure and relative humidity, respectively, on the capillary pressure computations. Figure 6 is a conceptual model showing the same drainage path as water saturation is decreased by vaporization processes. From pore throats 'a' through 'c', enough water is present to maintain a continuous wetting phase. Within these conditions, the cohesive force (attraction of like molecules) of the wetting phase is greater than the adhesive force created at the contact between the rock and the wetting phase. During the transition from 'b' to 'c', the adhesion force will cause the water molecules to spread across the maximum grain surface area, down to a single molecular layer. The Young-LaPlace equation is still appropriate through these stages since the water is still in a continuous distribution across the rock surface and cohesion forces are still significant. At this point the adhesion and cohesion forces are nearly balanced.

As the saturation state is reduced further by vapor desorption, the single layer of water molecules is broken, resulting in a non-continuous wetting phase. Part of the grain surface can be thought of as not having any wetting fluid in contact with the surface. At this point, the adhesion force is probably greater than the cohesion force of the water molecules. Effectively, the rock no longer has a continuous wetting phase, and the water saturation is in a sub capillary-equilibrium state. Under these conditions, the Kelvin equation, rather than the Young-LaPlace equation, is most appropriate. Parenthetically, the Kelvin equation is valid for all saturation ranges, but is most applicable in the low saturation region.

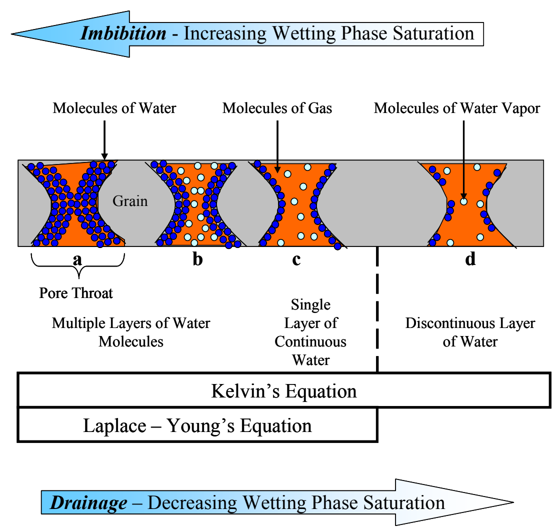


Fig. 6—Conceptual physical model illustrating the vapor desorption process and the saturation regions where each of the capillary pressure equations are most applicable.

Overview of Capillary Pressure Measurement Techniques

Capillary pressures and the associated wetting phase saturations are essential for the accurate evaluation of oil and gas reservoirs. Because of their unique gas storage and producing characteristics, accurate capillary pressures over the entire range of water saturations are especially critical for evaluating basin-centered gas systems. Capillary pressure measurements also provide basic descriptions of the reservoir rock, fluids and rock-fluid behavior. Capillary pressure data may be used to:

- estimate pore throat size distribution to classify hydraulic rock types;
- determine initial water saturation conditions;
- estimate water saturation, permeability, porosity, and height above free water level for reserve estimates;
- estimate absolute permeability;
- estimate seal capacity of the sealing facies; and
- estimate capillary pressure water saturation profiles.

There are four primary methods used by the petroleum industry to measure capillary pressure. These methods include high-speed centrifuge, high-pressure porous plate, high-pressure mercury injection, and vapor desorption. As described below, each method has basic advantages and disadvantages. Each of the measurement techniques is also applicable to very specific testing conditions. Finally, each technique is more appropriate for specific types of reservoir rocks.

Porous Plate Method.[21-24] The principal component of the porous plate method is a permeable membrane of uniform pore size distribution and containing pores of appropriate size such that the displacing fluid will not penetrate the membrane at some maximum pressure.[25] Capillary pressures are computed from the pressure increases required to displace fluid from increasingly smaller pores and pore structures.

The primary advantage of the porous plate method is the ability to test porous material using 'native' fluids and 'native-state' rocks. Consequently, it is not required to clean and dry samples before testing, thereby reducing the risk of either changing the *in-situ* wettability or altering intrinsic properties of the rock materials. This advantage is quite important in rocks containing significant clays and shales. Another advantage is the capability to test core samples without altering the intrinsic pore geometry or otherwise damaging the sample during testing.

The primary disadvantage of the porous plate method is a limitation on the highest capillary pressure that can be achieved. The upper limit of capillary pressure is controlled by the size of the largest pore throats in the membrane. Another significant limitation or disadvantage of the porous plate method is the long times required to reach equilibrium saturation levels. Both of these disadvantages limit or even preclude using the porous plate method in tight gas sands.

Centrifuge Method.[26-29] As the name implies, the centrifuge method de-saturates a core sample by imposing a centrifugal force on the sample, thus forcing the mobile phase out. The centrifugal force is created by rotating or spinning the core at increasingly higher speeds. The principal advantage of the centrifuge is the ability to obtain capillary pressure data very quickly relative to the porous plate method. Moreover, many high-speed centrifuges can now be operated at reservoir pressure and temperature conditions.

Similar to the porous plate method, the main disadvantage of the centrifuge method is the maximum pressure limitation. Most high-speed centrifuges are limited to a maximum capillary pressure of approximately 2000 psi. Another concern with the centrifuge technique is the uncertainty as to the distribution of the wetting phase fluid within the plug. Irregular wetting phase distributions can cause capillary end effects.[28] Yet another problem is related to cavitation, which occurs in gas-liquid systems when the air pressure is less than one atmosphere but the capillary pressure exceeds one atmosphere.[29] All of these phenomena may cause errors in the computed capillary pressures. In addition, the centrifuge is hindered by liquid evaporation during core preparation. Finally, we may be subject to measurement inaccuracies caused by very small displacement volumes.

High Pressure Mercury Injection Method.[30] High pressure mercury injection (MICP) involves injecting or forcing mercury into an evacuated core sample. The volume of mercury injected at each pressure determines the non-wetting (*i.e.*, mercury) saturation. This method is a very fast, often requiring only hours rather than days or weeks. Further, MICP is capable of attaining injection pressures as great as 60,000 psi, thus providing coverage of the entire range of water saturation and capillary pressure for both tight gas and high porosity and permeable rocks.

The disadvantages include the lack of a true wetting phase during testing. The test is performed on dry samples using mercury as the non-wetting phase fluid and assuming air is the wetting fluid. This requires conversion to reservoir conditions using contact angle and surface tension inputs. The oil and gas industry lacks standards for correcting the apparatus for system compressibility at high pressures (*e.g.* blank corrections) resulting in water saturation/capillary pressure distribution measurement errors. Finally, use of the contact angle and surface tension scaling parameters may not be appropriate for rocks with ultra-low water saturations and high capillary pressures or rocks with slot type pores, common to tight gas sand reservoirs.[7]

Vapor Desorption Method.[6-10] The fundamental principal of vapor desorption or vapor pressure lowering is the observation that the vapor pressure above a liquid's curved surface is a function of the liquid surface curvature. In addition, the capillary pressure is also a function of the liquid surface curvature. As a result, both capillary pressure and vapor pressure lowering are functions of the liquid saturation in a porous medium. Capillary pressures, therefore, are calculated from lowering the vapor pressure by controlling the relative humidity in the rock pores.

The relationship between the curvature of a gas-liquid interface and the vapor pressure of the liquid phase was first defined by Lord Kelvin in 1871.[31] As vapor pressure over a concave interface is reduced, the pressure reduction can be related to capillary pressure. The capillary pressure computed using the vapor pressure reduction process is frequently called the Kelvin capillary pressure. Melrose concluded that water vapor desorption is a valid technique for obtaining capillary pressure when using the classic or corrected form of the Kelvin equation.[6]

Vapor pressure reduction can be controlled with humidity chambers where relative humidity and the subsequent saturation equilibrium is controlled with various concentrations of salts in a liquid solution.[6-10] The primary advantage of this method is the ability to achieve very high capillary pressures as well as very low water saturations. Melrose used various salt solutions to decrease the vapor pressure on core samples in a humidity chamber, resulting in capillary pressures as high as 4000 psi for an air/brine system.[6] We have achieved gas/water capillary pressures in excess of 10,000 psi and water saturations below 5%. As a result, this technique is especially suited for reservoir systems characterized by ultra-low water saturations and abnormally high capillary pressures like the Bossier sands.

The vapor desorption measurement precision decreases, however, at very high relative humidity (>95%) which limits the lower limit of capillary pressure to a range somewhere between 500 to 1000 psi. Consequently, a disadvantage of the vapor desorption technique is the ability to measure capillary pressures at high water saturations. Similar to the porous plate method, another limitation is the time required to achieve equilibrium.

Laboratory Program: Materials and Protocols

Materials. Capillary pressures were measured using both vapor desorption and centrifuge methods on six core samples taken from the Bossier sands. These plugs were taken from a whole core obtained with an oil-base mud program in an attempt to quantify initial connate water saturations more accurately. We attempted to sample from a range of hydraulic rock types that we believe comprise reservoir quality rocks in the Bossier sands. Table 1 lists the six sand samples used in the laboratory measurements and their basic intrinsic properties. Note that both porosity and Klinkenberg-corrected permeability were obtained at a net overburden pressure of 800 psig.

Effective porosity ranged from 4.9% to almost 14%, while the Klinkenberg-corrected permeability varied from 0.0006 md to 0.143 md. The range of initial water saturation, as measured by Dean-Stark extraction process, was from 5% to 45% with an average of 21%. The range of hydraulic rock types was 2A to 3, representing the best to worst reservoir quality rocks. Generally, initial water saturation increases with a decrease in the rock quality.

Table 1-Summary of Intrinsic Rock Properties and Hydraulic Rock Types for Test Samples

Sample No.	Effective Porosity (%)	Klinkenberg-Corrected Permeability (md)	Connate Water Saturation (%)	Hydraulic Rock Type
1-26	5.3	0.0040	41.5	3A
2-28	4.9	0.0006	44.5	3A
2-32	8.4	0.0850	19.2	2A
3-17	13.8	0.1430	5.3	2A
3-42	13.0	0.0410	11.6	2B
4-18	8.7	0.0066	6.7	3A

Procedures. Prior to making any measurements, the cores were cleaned and dried. We used a low-temperature azeotropic (chloroform-methanol) solution with a Dean Stark extraction process to clean the cores. The samples were then dried in a humidity-controlled environment.

All capillary pressures were measured using a drainage process (*i.e.*, water saturations decreasing). The testing sequence began by first measuring capillary pressure using the centrifuge method. Samples were fully saturated with synthetic brine having a NaCl concentration of 5,000 ppm. Centrifuge capillary pressure was measured at four pressure steps: 100, 200, 400 and 1000 psi. Water saturation was estimated using the Hassler-Brunner method.[26] The minimum centrifuged water saturations that were attained ranged from 11.5% to 76.8% at a maximum pressure of 1,000 psig. In general, the best quality reservoir rocks (*i.e.*, hydraulic rock types 2A) had the lowest saturations, while the poorest quality reservoir rock (*i.e.*, hydraulic rock type 3A) had the highest.

Capillary pressure was then measured using a vapor desorption method. Rather than use various types and concentrations of salt solutions to control vapor pressure, we used a humidity chamber with temperature controls. Temperature was maintained at 30^{o}C for all measurements. We began at the highest relative humidity and reduced the value in a step-wise fashion at all subsequent measurements. This particular test sequence also represents a drainage type test where the wetting phase saturation is reduced as the humidity of the chamber is reduced, resulting in an increase in the computed capillary pressure. Core samples were weighed periodically to determine when equilibrium water saturation was achieved at each relative humidity step. The time duration required to reach equilibrium for each humidity step increased with each increase in relative humidity. Water saturation was determined by gravimetric techniques, and capillary pressure was computed using the classic form of the Kelvin equation defined by Equation (2).

Results of Laboratory Measurements

Capillary pressures measured using both vapor desorption and centrifuge methods are shown in Cartesian and semilog plots in Figures 7a and 7b, respectively. The color-filled triangles represent data from the centrifuge method, while color-filled circles are from the vapor desorption technique. The centrifuge data were obtained primarily to validate measurements from the vapor desorption technique, especially at the higher water saturation range.

All data were obtained with a drainage (*i.e.*, decreasing water saturation) process. Differences among the curves are indicative of the variation in core properties, including variations in the pore throat aperture distribution. Rocks containing a greater frequency of small pore throats will have a greater entry and displacement pressure and will typically be characterized by lower permeability.

Note that we were able to achieve gas-water capillary pressures in excess of 10,000 psi and water saturations below 5% with the vapor desorption method. The Cartesian plot (Fig. 7a) provides more details at the high capillary pressure and low water saturation range, while the semi-log plot (Fig. 7b) yields more detail in the low capillary pressure and high water saturation range. Although there is no direct overlap or connection between the vapor desorption and centrifuge data, they do appear to follow a consistent trend, thus validating the vapor desorption measurements. The composite drainage curve provides full coverage of entire saturation range.

Continuity Between Vapor Desorption and Centrifuge Capillary Pressure Measurements. The centrifuge data provides coverage of capillary pressure in a higher water saturation and lower capillary pressure range than the vapor desorption method. Several previous studies comparing capillary pressures obtained from different methods show an overlap in some data. Although we do not see any such overlap in our data, we do observe a very clear and obvious continuity in the composite capillary pressure curves generated for each rock type. The merged data satisfactorily provide drainage curves that span the complete saturation range. This continuity provides confidence that the vapor desorption method provides an accurate description of the saturation distribution for all rock types tested in the low saturation and high capillary pressure region of the capillary pressure curve.

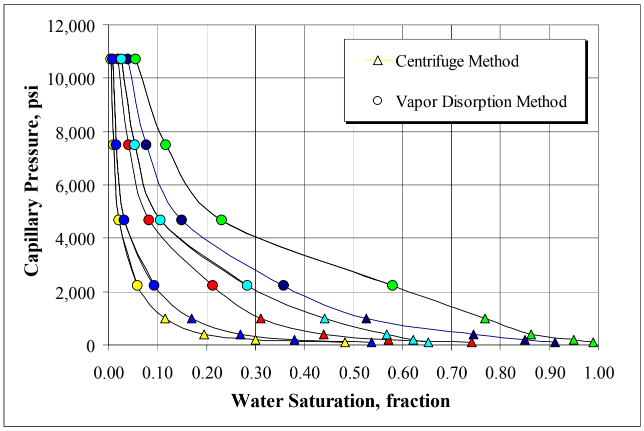


Fig. 7a—Cartesian plot of the capillary pressures derived from both centrifuge (triangles) and vapor desorption (circles).

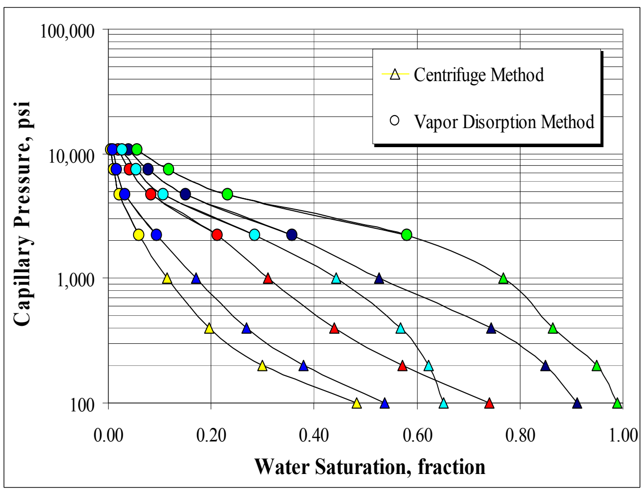


Fig. 7b—Semi-log plot of the centrifuge and vapor desorption drainage capillary pressure curves.

Changes in Brine Salinity During Vapor Desorption Measurements. Figures 8a and 8b show the increase in both the brine salinity and brine ratio with each relative humidity step, respectively. We define the brine ratio as the residual brine at the end of each humidity step divided by the initial brine salinity. Recall that all cores were initially saturated with a synethetic brine with 5,000 ppm NaCl. Note that as each sample is exposed to lower relative humidity environments, the liquid pore water is vaporized, thus causing the NaCl concentration to increase in the remaining pore waters.

As shown in Fig. 8a, Sample 3-42 exhibited the greatest increase in salinity, exceeding 100,000 ppm after only four relative humidity steps. The pore water salinity for this sample began to increase at a critical relative humidity, somewhere less than 80%. The results also indicate that the salinization of the residual pore water occurs rapidly in the vapor desorption process. Another way to express this is to compare the salinity after each relative humidity step to the initial salinity of 5000 ppm. All samples had salinity increases greater than an order of magnitude from the original. Increases in salinity ranged from a factor of greater than 10 to more than 20 times the salinity of the original pore water.

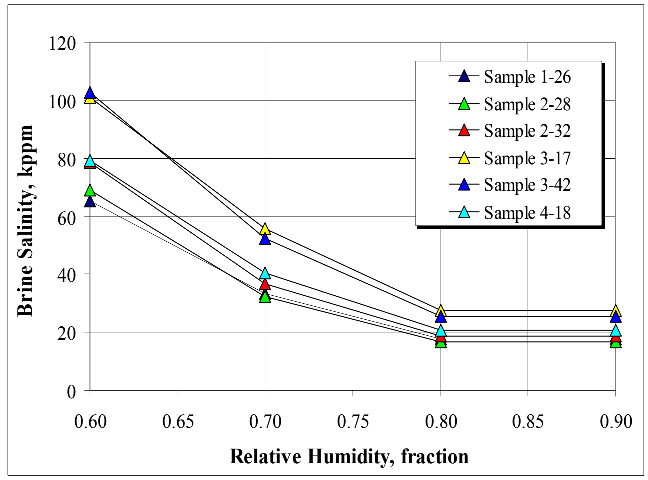
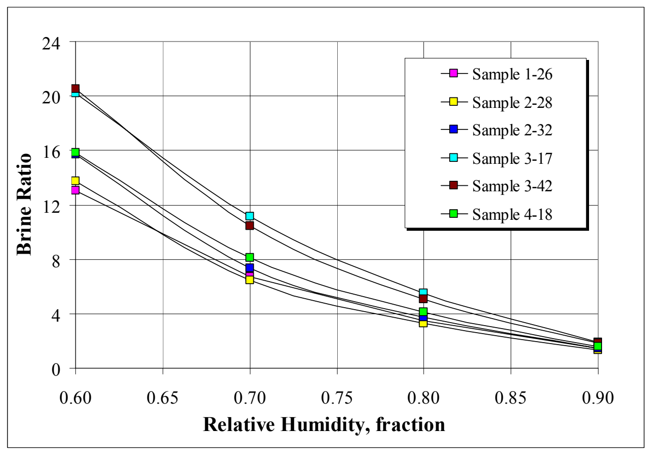


Fig. 8a—Relative humidity vs. brine salinity after each relative humidity step was completed.



Fig, 8b—Relative humidity vs. brine ratio after each relative humidity step was completed.

Vapor Desorption Process: Laboratory *vs.* Field Conditions. Questions for which we desired answers before beginning this study include:

- Can the vaporization process that is proposed in the sub capillary equilibrium hypothesis[1] be duplicated in the laboratory?
- Can the observed high capillary pressure and low water saturations also be created by the vapor desorption process on rock samples in the lab?
- Does the vapor desorption process provide a mechanism to cause formation salinity to increase from normal marine conditions (~25,000 to 35,000 ppm) to the present day salinity range of 180,000 ppm to 300,000 ppm?

Our findings clearly show that both low water saturation and high capillary pressure can be achieved in the laboratory using the vapor desorption method. The drainage process created by the vapor desorption test is believed to be very similar to the drainage process responsible for dewatering the Bossier sands to a sub capillary-equilibrium condition. The primary difference between reservoir and lab conditions is that at reservoir conditions, the water molecules vaporize into the natural hydrocarbon gases, rather than air, as in the humidity chamber.

The Bossier sands were found to contain very high concentration of NaCl, ranging from 180,000 ppm to 300,000 ppm. In every sample, the brine salinity increased from an initial condition of 5000 ppm to as much as 102,000 ppm at the last humidity step. The brine ratio also showed increases of between 13 to 21 times the original salinity. So it appears that vapor desorption provides a mechanism to concentrate formation water salinity to present day conditions. We believe that if the tests began with a brine salinity that more closely matched sea water (~35,000 ppm), the final salinity would have been much closer to that measured in the Bossier sands. Concerns about precipitating NaCl in the samples during the desorption tests prevented us from starting at this higher initial salinity.

We believe that the attributes of ultra-low water saturation, abnormally high capillary pressure, and increased salinization of the residual connate waters are related to the vapor desorption process in the Bossier tight gas sands of East Texas. We have duplicated the process in the laboratory and found the results to be consistent with the observations and measurements made on the Bossier reservoir rocks.

Conclusions

On the basis of our study of capillary pressure measurements using a vapor desorption technique in the Bossier tight gas sands, we offer the following conclusions:

1. Laboratory tests on core samples using the vapor desorption capillary pressure method were consistent with capillary pressure measurements using a centrifuge method. The two methods were found to be in continuum at their measurement intersection pressure range of 1000-2000 psi for the six samples tested.

2. The vapor desorption method provides an alternate method for extending capillary pressure measurements into the high pressure and ultra-low water saturation range consistent with the Bossier tight gas sands.

3. The low water saturations achieved at high capillary pressures are consistent with the low water saturation measured from the core extractions and the log-based estimates in the Bossier sands in the Mimms Creek Field.

4. The laboratory-based vapor desorption process mimics a field-based mechanism that causes in-situ connate water to become more saline through time as hydrocarbon gases flow through the system and vaporize the liquid water. We propose that this is the process responsible for the high formation water salinity measured in the Bossier tight gas sands in East Texas.

5. The vapor desorption process is also a plausible mechanism for creating the sub capillary equilibrium water saturation distribution[5] observed in the Bossier tight gas sands of the Mimms Field of East Texas.

Nomenclature

P_c = capillary pressure, psi
P_{nw} = pressure of the non-wetting phase, psi
P_w = pressure of the wetting phase, psi
r = capillary radius, μ
σ = interfacial tension, dynes/cm
RH = relative humidity
R = universal gas constant, 8.314 J/Mol K
T = absolute temperature, degrees Kelvin
V_m = molar volume of water
p_2 = partial vapor pressure for brine within the sample
p_4 = partial vapor pressure for salt solution

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References

1. Prouty, J.L.: "Tight Gas in the Spotlight," in *GasTIPS*, Gavin, J.J. and Lang, K.R. (Editors), Gas Technology Institute, vol. 7, no. 2, Chicago, IL (2001), pg 4-10.
2. Gwilliam, B. and Nuccio, V.F.: "Basin-Centered Gas Systems of the U.S.," U.S. Department of Energy, National Energy Technology Laboratory, Report DE-AT26-98FT40031, April 1998-November 2000.
3. Law, B.E.: "What Is A Basin-Centered Gas System?," paper presented at the Rocky Mountain Association of Geologists 2000 Basin-Centered Gas Symposium, Denver, CO, October 6.
4. Emme, J.J. and Stancil, R.W.: "Anadarko's Bossier Gas Play—A Sleeping Giant in a Mature Basin," Abstract, AAPG *Bulletin*., v. 86, no. 13, Supplement (2002).
5. Newsham, K. E. and Rushing, J. A.: "Laboratory and Field Observations of an Apparent Sub Capillary-Equilibrium Water Saturation Distribution in a Tight Gas Sand Reservoir," paper SPE 75710 presented at the 2002 SPE Gas Technology Symposium, Calgary, Alberta, Canada, April 5-8.
6. Melrose, J.C.: "Use of Water Vapor Desorption Data in the Determination of Capillary Pressure," paper SPE 16286 presented at the 1987 SPE International Symposium on Oilfield Chemistry, San Antonio, TX, Feb. 4-6.
7. Melrose, J.C.: "Valid Capillary Pressure Data at Low Wetting-Phase Saturation," *SPE Reservoir Engineering* (Feb. 1990), pp 95-100.
8. Melrose, J.C., Dixon, J.R., and Malison, J.E.: "Comparison of Different Techniques For Obtaining Capillary Pressure Data In the Low Saturation Range," paper SPE 22690 presented at the 1991 SPE Annual Technical Conference and Exhibition, Dallas, TX, Oct. 6-9.
9. Morrow, N.R., Brower, K.R., and Kilmer, N.H.: "Relationships of Pore Structure to Fluid Behavior in Low Permeability Gas Sands", Final Report, DOE/BC/10216-13 (DE84012721), U.S.

Dept. of Energy, Bartlesville (Sept., 1984), 60-71.
10. Ward, J.S., and Morrow, N.R.: "Capillary Pressure and Gas Relative Permeabilites of Low Permeable Sandstone", paper SPE/DOE 13882 presented at the 1985 SPE/DOE Symposium on Low Permeability Reservoirs, Denver, CO, May, 1985.
11. Montgomery, S.: "East Texas Basin Bossier Gas Play," in *Petroleum Frontiers*, Anderson, J., ed., IHS Energy Group, Englewood CO (2000), pp 1-60.
12. Gunter, G.W*., et al*..: "Early Determination of Reservoir Flow Units Using an Integrated Petrophysical Model," paper SPE 38679 presented at the 1997 SPE Annual Technical Conference and Exhibition, San Antonio, TX, October 5-8.
13. Newsham, K.E. and Rushing, J.A.: "An Integrated Work-Flow Model to Characterize Unconventional Gas Resources: Part I-Geological Assessment and Petrophysical Evaluation," paper SPE 71351 presented at the 2001 SPE Annual Technical Conference and Exhibition, New Orleans, LA, September 30-October 3.
14. Folk, R.L.: *Petrology of Sedimentary Rocks*, Hemphill Publishing Co., Austin, TX, 1974.
15. Washburn, E. W.: "Note On A Method of Determining the Distribution of Pore Sizes In A Porous Material", *Proc*., The National Academy of Science (1921), v. 7, p.115-116.
16. Swanson, B. F.: "A Simple Correlation Between Permeabilities and Mercury Capillary Pressure", paper SPE 8234 presented at the 1979 SPE Annual Technical Conference and Exhibition, Las Vegas, NV, Sept. 23-26.
17. Thompson, A. H., *et al*.: "Estimation of Absolute Permeability From Capillary Pressure Measurements", paper SPE 16794 presented at the 1987 SPE Annual Technical Conference and Exhibition, Dallas, TX, Sept. 27-30.
18. Pittman, E. D.: "Relationship of Porosity and Permeability to Various Parameters Derived From Mercury Injection-Capillary Pressure Curves for Sandstone", AAPG *Bull*., (Feb. 1992), v. 76, No. 2, p. 191-198.
19. Collins, R.E.: *Flow of Fluids Through Porous Materials,* The Petroleum Publishing Co., Tulsa, OK (1976), pp 33-36.
20. Calhoun, J.C., Jr., *et al*. "Experiments on the Capillary Properties of Porous Solids," *Trans.* AIME, vol. 186 (1949), pp 189-196.
21. McCullough, F.W., *et al*.: "Determination of the Interstitial-Water Content of Oil and Gas Sand by Laboratory Tests of Core Samples," *Drill. & Prod. Prac.* API (1944), pp 180-188.
25. Amyx, J.W., Bass, D.M., Jr., and Whiting, R.L.: *Petroleum Reservoir Engineering: Physical Properties*, McGraw-Hill Book Co., New York, NY (1960).
22. Thornton, O.F. and Marshall, D.L.: "Estimating Interstitial Water by the Capillary Pressure Method," *Trans*. AIME, vol. 170 (1947), pp 69-80.
23. Bruce, W.A. and Welge, H.J.: "Restored-State Method for Determination of Oil-in-Place and Connate Water," *Oil & Gas J*., vol. 46 (1947), pp 22-23.
24. Rose, W. and Bruce, W.A.: "Evaluation of Capillary Character in Petroleum Reservoir Rock," *Trans*. AIME, vol. 186 (1949), pp 127-142.
26. Hassler, G.L. and Brunner, E.: "Measurement of Capillary Pressures in Small Core Samples," *Trans*. AIME, vol. 160 (1945), pp 113-144.
27. Slobod, R.L., *et al*.: "Use of Centrifuge for Determining Connate Water, Residual Oil, and Capillary Pressure Curves of Small Core Samples," *Trans.* AIME, vol. 192 (1951), pp 127-134.
28. O'Meara, D.J., Jr., *et al*.: "Centrifuge Measurments of Capillary Pressure: Part 1-Outflow Boundary Condition," paper SPE 18296 presented at the 1988 SPE Annual Technical Conference and Exhibition, Houston, TX, October 2-5.
29. Hirasaki, G.J., *et al*.: "Centrifuge Measurments of Capillary Pressure: Part 1-Cavitation," paper SPE 18592 presented at the 1988 SPE Annual Technical Conference and Exhibition, Houston, TX, October 2-5.
30. Purcell, W.R.: "Capillary Pressures-Their Measurement Using Mercury and the Calculation of Permeability Therefrom," *Trans.* AIME, vol. 186 (1949), pp 39-48.
31. Thomson, W. (Lord Kelvin), "On the Equilibrium if Vapour at a Curved Surface of Liquid", *Proc*., Roy. Soc. Edinburgh, 1870, 7, 63-67; Phil. Mag. (1871), Ser. 4, 42, 448-452.