

THE ROLE OF BOUND WATER AND CAPILLARY WATER IN THE EVALUATION OF POROSITY IN RESERVOIR ROCKS

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Abstract Knowledge of the quantity and distribution of the different types of water contained within the interconnected pore volume of a reservoir rock is fundamental to formation evaluation. Three main water types have been identified as bound, capillary and free waters. Bound water includes both water held to the net-negatively charged mineral surfaces, and the water of hydration associated with the mineral charge balancing counter-ions. Capillary water is immobile water held by capillary forces in regions of microporosity, for example dead end pores and pendular rings. Free water is water that is able to flow under a given pressure gradient.

A new laboratory technique, thermogravimetry/evolved water analysis TG/EWA, has been used to quantify these different water types. Bound/capillary water relationships are presented for core taken from three different North Sea reservoirs that exhibit very different clay mineralogy. Berea sandstone was included in the study. The data have been integrated with measurements of porosity, surface area, mercury porosimetry, SEM and XRD to explain the influence that rock structure and mineralogy have on the quantity and distribution of water types. All the rocks studied contain much more capillary held water than bound water. The amounts held are strongly dependent on the type of clay mineral that predominates, along with its morphology and location within the pore system. This study has shown that reservoir rocks that contain chlorite as the major clay mineral can hold up to 10 times more capillary water than bound water.

INTRODUCTION

Porosity is an important parameter for the calculation of hydrocarbon reserves in reservoir evaluation. Hence it is necessary to understand what controls the distribution of water, and therefore hydrocarbons, held within the interconnected porosity. In porous media three types of water have been identified as free, capillary and bound. Free water is able to flow under an applied pressure

gradient. Capillary water is immobile water held by capillary forces in regions of microporosity, for example dead-end pores and pendular rings. Bound water includes both the water strongly held to negatively charged clay mineral surfaces, and the water of hydration associated with the mineral charge-balancing cations.

In an ideal porous medium of high porosity with smooth pore walls, a large proportion of the pore water would be free water. In this type of pore system, water will drain by the application of a pressure gradient, thus removing free water from the centre of the pores, leaving a small amount of capillary water in pendular rings and bound water on the mineral surfaces. In reality, however, most reservoir sandstones contain clay minerals which are associated with zones of microporosity. Water is held within these microporous regions, mainly by capillary forces, and in reservoir rocks this capillary water may constitute a significant fraction of the total pore volume. Relatively small amounts of water are also bound to the surface of the clay minerals by forces of electrostatic attraction.

The purpose of this paper is to provide a preliminary insight into the influence that both capillary-held and bound water have upon the petrophysical determination of porosity in reservoir sandstones. A key factor in this study is the quantification of the different types of water by the new laboratory technique of thermogravimetry/evolved water analysis. The evaluation process also draws upon measurements of porosity, surface area, mercury porosimetry, scanning electron microscopy and clay mineralogy. The aim is to appraise the distribution of water in sandstones in order to gain an improved understanding of the porosity and water saturation as obtained from core analysis and wireline logs.

WATER TYPES

Bound Water

As the name implies, bound water is the least mobile of the three water "types", and is essentially held close to the surface of the rock matrix. Because of their small size relative to framework grains, clay minerals contribute the major fraction of total surface area exposed to pore fluids. Bound water is therefore mainly associated with the surfaces of clay minerals.

The basal surfaces of most clay minerals exhibit a net-negative charge which arises from isomorphous substitution in the clay mineral sheets. This occurs when an element of higher valency is replaced by one of a lower valency, eg by substitution of Al^{3+} for Si^{4+} . Water is held to the negatively charged basal surfaces by the mechanism of hydrogen bonding.

Water may also be bound to the broken bonds associated with the edges of the clay mineral crystals and by ion-dipole hydration of the charge-balancing cations. The different mechanisms by which the water may be bound are all interlinked, therefore making it difficult to distinguish experimentally between them.

The amount of bound water associated with the surface of clay minerals has been studied using a variety of techniques which include nuclear magnetic resonance (NMR) and electron spin resonance (ESR). This subject has recently been reviewed by Newman (1987) who concluded that the influence of the clay surface on the ordering of water molecules does not extend much further than the second or third layer of molecules and that beyond this distance water appears to behave as a true liquid. As the diameter of a water molecule is 0.28nm, the approximate thickness of the bound water layer according to Newman is between 0.56nm and 0.84nm.

Capillary Water

Capillary water is essentially immobile and is retained in the very small pore spaces between the clay mineral crystals by capillary forces. Water may also be held by capillary forces in pendular rings around the regions of grain-to-grain contacts.

Free Water

Free water in reservoir rocks resides mainly within the macroporous regions of the interconnected pore space. This type of water is able to drain by the application of a pressure gradient.

WATER VAPOUR SORPTION ISOTHERMS

Adsorption/desorption isotherms of water vapour may be used to investigate the bound/capillary water relationships of reservoir rocks. The following discussion provides a basis for understanding the water vapour sorption processes.

The amount of water adsorbed within the pore space of the rock is measured at a series of relative vapour pressures (RVP) under isothermal conditions. Relative vapour pressure = P/P_0 , where P is the vapour pressure of water and P_0 is the saturated vapour pressure of water.

A water vapour adsorption isotherm for a non-porous oxide material (Hagymassy, 1969) is shown in Figure 1, in which the amount of water adsorbed is shown as a function of relative vapour pressure. To aid interpretation, the amount adsorbed is expressed in terms of a statistical number of monolayers. The initial portion of the isotherm shows a sharp upward trend in which water is strongly adsorbed to the surface of the sample. The amount adsorbed then increases more slowly as relative vapour pressure is increased and a knee in the isotherm is seen which is commonly referred to as point B, the point at which monolayer coverage is complete.

By analysing the region of the isotherm up to a relative vapour pressure of 0.3, using the Brunauer, Emmett and Teller (BET) theory (Gregg, 1982), monolayer coverage may be assessed. Taking the cross-sectional area of a water molecule as 0.106nm^2 (Mc Clellan, 1967), the surface area of the material may be calculated.

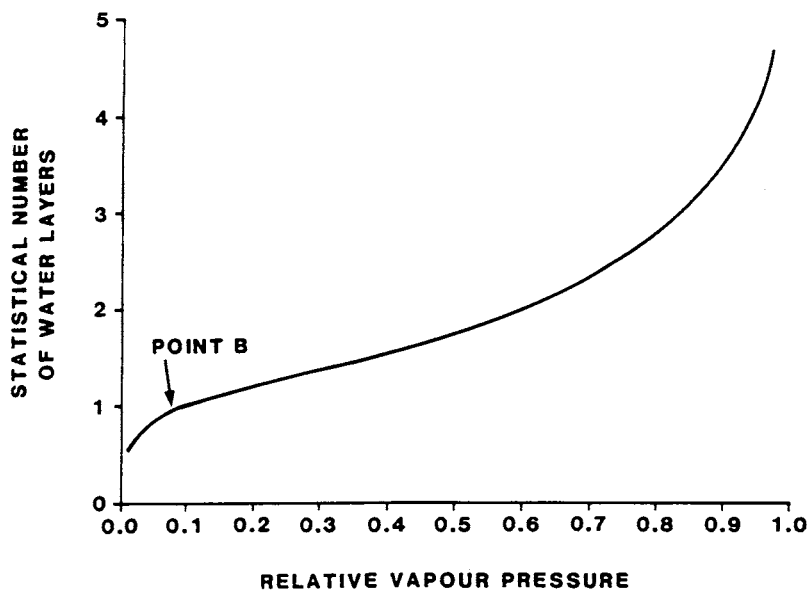


FIGURE 1 Water vapour adsorption isotherm
(After Hagymassy et al., 1969).

At 0.55 RVP approximately two monolayers of water are adsorbed on non-porous oxide materials. Multilayer adsorption then continues as the relative vapour pressure is increased and at 0.9735 RVP approximately five layers of water molecules are adsorbed onto the surface of the sample.

If the thickness of one layer of water molecules is 0.28nm then at 0.55 RVP the thickness of the water film would be approximately 0.56nm and at 0.9735 RVP, approximately 1.4nm.

Water vapour sorption studies have also been carried out on the clay minerals kaolinite (Martin, 1958) and illite (Branson, 1983). The shape of the isotherms on these minerals are very similar to those obtained on non-porous oxide materials and at 0.55 RVP approximately two monolayers of water are adsorbed.

An adsorption isotherm measured on a porous medium that exhibits no microporosity, ie all pores above 1 μm diameter, would be similar in shape to that obtained on a non-porous material. Conditions of 0.998 RVP are required before pores of 1 μm diameter are filled by the process of capillary condensation.

Reservoir rocks that contain microporosity exhibit similar adsorption characteristics in the initial part of the adsorption isotherm. However above a relative pressure of approximately 0.55 (Figure 1), capillary condensation of water commences in the smallest pores. The number of water layers adsorbed then increases over and above the number that would be adsorbed on a non-microporous rock of the same surface area. As the relative vapour pressure is increased progressively, wider and wider pores are filled with liquid water.

The relationship between relative vapour pressure and the radius of a cylindrical pore may be described by the Kelvin equation (Gregg, 1982):

$$\ln(P/P_0) = -2\gamma V/RT r, \quad (1)$$

where P/P_0 = relative vapour pressure,
 γ = interfacial tension,
 V = molar volume,
 R = gas constant,
 T = temperature,
 r = radius of a cylindrical pore.

Capillary pressure is related to the radius of a cylindrical pore through the expression

$$P_c = 2\gamma \cos \theta / r.$$

Where θ is the contact angle between the pore surface and the liquid meniscus. As the contact angle between the liquid meniscus and solid mineral surface is zero, $\cos \theta = 1$, and

$$r = 2\gamma / P_c. \quad (2)$$

By substituting for r in equation (1), relative vapour pressure may be related to capillary pressure by

$$\ln(P/P_0) = -P_c V / RT.$$

or
$$P_c = -\ln(P/P_0) RT / V. \quad (3)$$

BOUND/FREE CAPILLARY WATER RELATIONSHIPS

Bound/capillary water relationships have been studied by determining quantitatively the amounts of water desorbed from reservoir rocks that have been prepared under the specific conditions of 0.55 RVP and 0.9735 RVP, using the new technique of TG/EWA.

At 0.55 RVP approximately 2 to 3 monolayers of water are adsorbed onto the rock mineral surfaces. This amount of water is used in this study to represent the amount of "bound" water.

The amount of "capillary" water is determined from samples that have been equilibrated at 0.9735 RVP. From equation (1), at 0.9735 RVP pores of up to 0.080 μm diameter are filled with liquid water. Using equation (3), the equivalent air/water capillary pressure under these conditions is 3.63 MPa (527 psi). However, such high capillary pressures are rarely encountered in the reservoir and this amount of water is taken to represent a minimum value for "capillary" held water.

Samples Studied

Core samples from three different North Sea reservoirs have been studied which are referred to throughout the text as sandstones A, B and C. The porosity of the core from all three reservoirs is similar, ranging from 20% to 27%, however the individual reservoirs exhibit very different clay mineralogy. Berea sandstone was included in the study as it is well characterised and widely used as a reference material in core analysis research.

THERMOGRAVIMETRY/EVOLVED WATER ANALYSIS (TG/EWA)

The new laboratory technique of TG/EWA has been used to quantify accurately the amount of water desorbed from prepared reservoir core samples. A schematic of the instrument is shown in Figure 2. A high precision Cahn electrobalance records continuously the weight loss of a sample as it is heated at a controlled rate. Dry nitrogen carrier gas is passed around the sample which is located within a furnace. Water released from the sample is transferred with the carrier gas through the base of the furnace to a specific infra-red water vapour analyser, which monitors the concentration of water vapour in the evolved gas stream (Morgan, 1977).

Sample Preparation

The original pore fluids, oil and brine, were removed from the core samples by miscible cold solvent cleaning using alternating cycles of methanol/toluene at ambient temperature. From a final washing in methanol the samples were immersed in simulated formation brine at 1/20 dilution. This was carried out to ensure that the different cations adsorbed onto the clay mineral surfaces were present in the same relative proportions as in the reservoir. After soaking for several days the samples were then given a further two soakings in very weak 50 ppm simulated formation brine to remove excess cations.

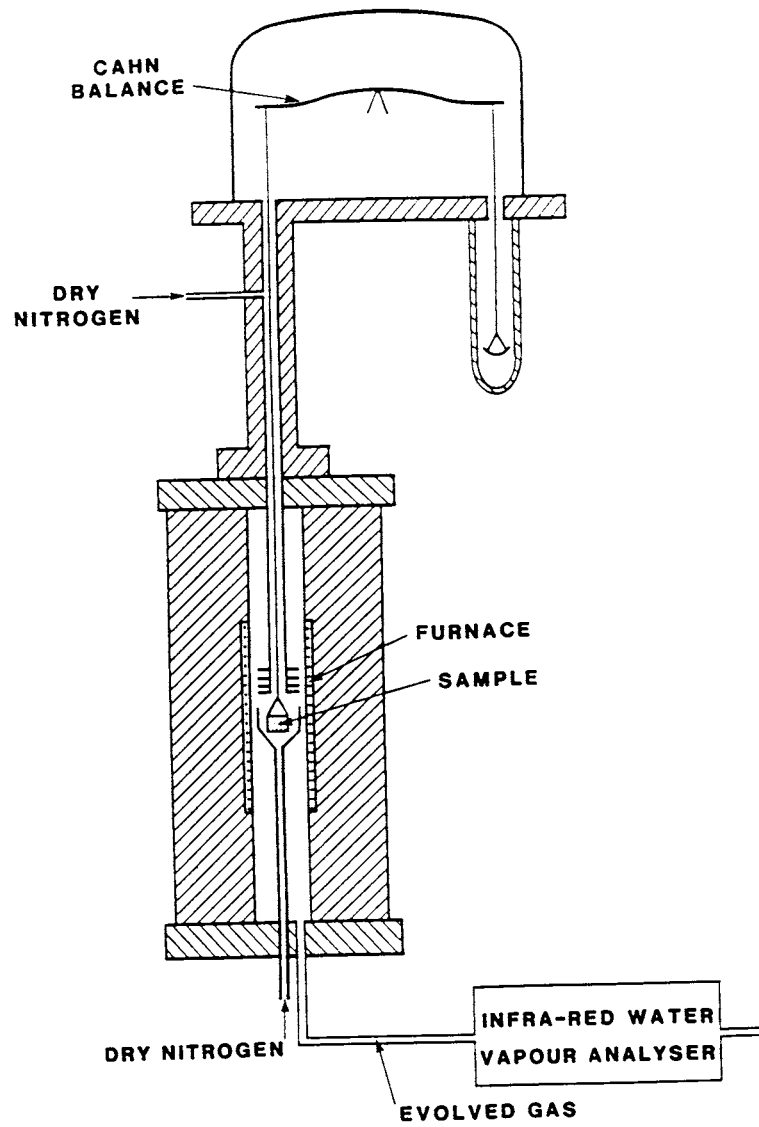


FIGURE 2 Schematic of thermogravimetric/evolved water analysis (TG/EWA) instrument.

After draining excess surface fluid, one core section of each sample was equilibrated in a vacuum dessicator over a saturated salt solution of magnesium nitrate at 20 °C, equivalent to an environment of 0.55 RVP, (Branson, 1983). The second core section was equilibrated over a saturated solution of potassium sulphate at 20 °C, equivalent to an environment of 0.9735 RVP. (Melrose, 1987). The samples were left in the vacuum dessicators for a minimum of one month to attain constant weight.

Measurement Procedure

The prepared reservoir rock was weighed into the sample pan of the Cahn electrobalance. Dry nitrogen carrier gas was passed at a constant rate through the furnace and sample area. The amount of water evolved from the sample whilst heating to 200 °C was monitored continuously, both by weight loss and by measuring the concentration of water vapour in the evolved gas stream. All adsorbed water was removed under these conditions.

Clay minerals contain hydroxyl groups as an integral part of their structure which, on heating between 300 °C and 900 °C, are lost in the form of water. Clay mineral dehydroxylation does not occur under the experimental conditions used in this work because the core samples were not heated above 200 °C.

OTHER MEASUREMENTS

Offcuts were prepared by miscible cold solvent cleaning followed by vacuum oven drying at 60 °C. Oven drying of the miscibly cleaned preserved samples does not alter the clay morphology of the sandstones studied and therefore critical point drying was not required (Pallatt, 1984).

X-ray diffraction (XRD) analysis was used to determine the relative proportions of clay minerals in the separated <5 μm size fraction of selected samples. The technique of low temperature krypton adsorption was used to measure surface area (SA), and the pore size distribution (PSD) was determined by mercury porosimetry. Scanning electron microscopy (SEM) was used to examine the morphology and the location of the clay minerals within the pore system.

RESULTS

X-ray diffraction data of the separated <5 μm size fraction, expressed in terms of relative proportions of clay minerals, are shown in Table 1.

TABLE 1 X-Ray Diffraction Analysis (<5 μ m size fraction).

Sandstone	Kaolinite %	Illite %	Chlorite %
A	73	15	12
B	-	97	3
C	3	30	67
Berea	81	12	7

Scanning electron microscopy was used to determine the morphology and location of the clay minerals within the pore system. Figure 3 shows that sandstone A contains kaolinite, a pore filling clay mineral which creates very few regions of microporosity due to its large particle size and random distribution within the pore system.

Figure 4 shows the clay mineral illite in sandstone B which occurs as an open tangled web of long thin ribbons that bridge the pore channels and coat much of the pore surface. The small distances between the ribbons create gross regions of microporosity in which water is held by capillary forces.

Figure 5 shows chlorite in sandstone C. This clay mineral occurs as thin, platy crystals that grow perpendicular to and coat the quartz framework grains. The distance between the individual chlorite platelets is typically <1 μ m across.

Figure 6 shows a chlorite grain coating that has become separated from a sandstone grain. The photomicrograph illustrates that these chlorite platelets can protrude up to 10 μ m out into the pore space, thus creating gross regions of microporosity in which large amounts of water may be held by capillary forces. The location of chlorite around the perimeter of the framework grains leaves an open permeable region of pore space beyond the tips of the crystals where, in a reservoir sandstone, hydrocarbons would be located. Under an applied pressure gradient, hydrocarbons will flow through these larger pore spaces, and water will be retained by capillary forces in the microporous regions between the chlorite platelets.

Typical mercury intrusion PSD profiles are shown in Figure 7. The data are plotted as incremental change in pore volume relative to that in the log of the mean pore throat diameter vs log of the mean pore throat diameter. With this plot, the area under the curve is directly related to the pore volume.

BET krypton and water surface areas are compared in Table 2. The surface area to water was calculated using the amount of water desorbed during TG/EWA from samples prepared at 0.55 RVP, assuming a 2 monolayer coverage under these conditions.

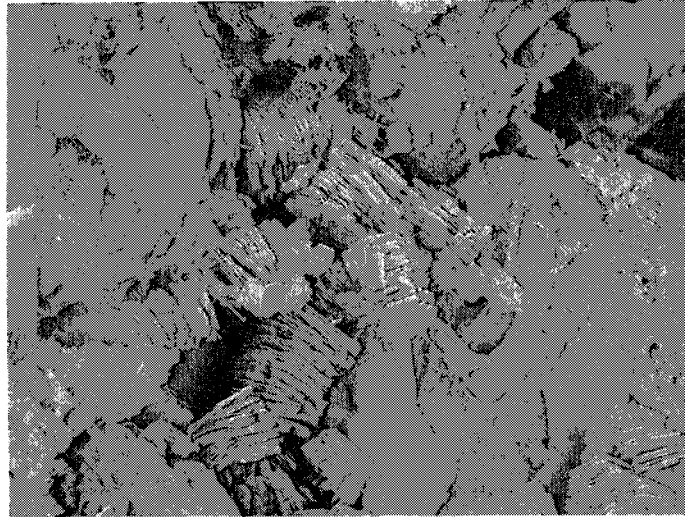


FIGURE 3 Sandstone A (Kaolinite)

10 μ m

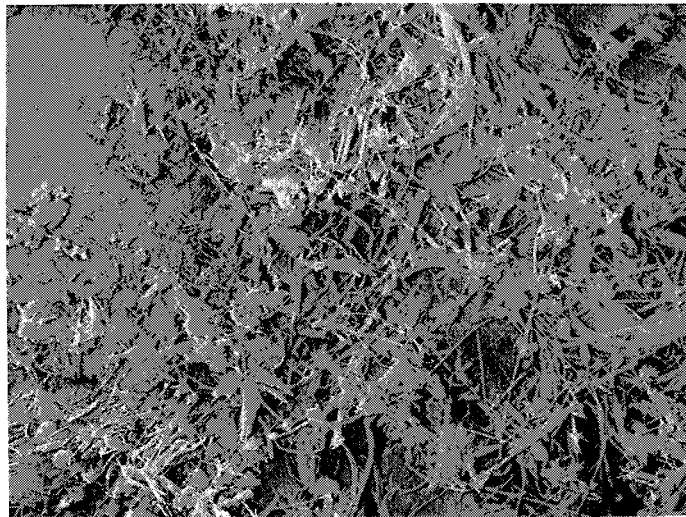


FIGURE 4 Sandstone B (Illite)

10 μ m

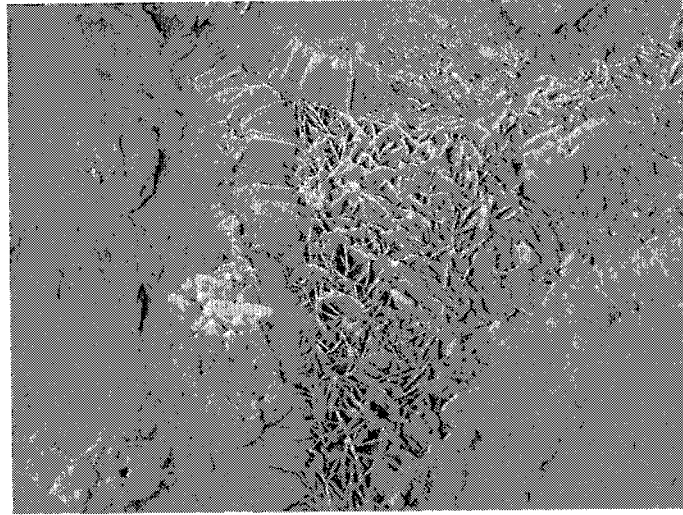


FIGURE 5 Sandstone C (Chlorite).

10μm

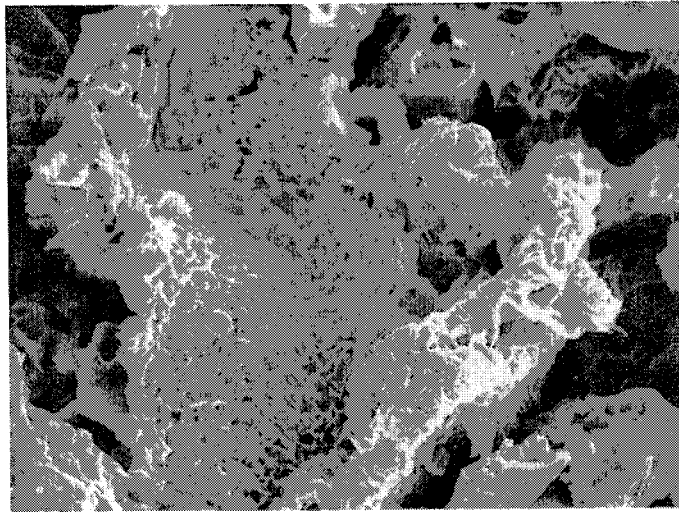


FIGURE 6 Sandstone C (Chlorite).

10μm

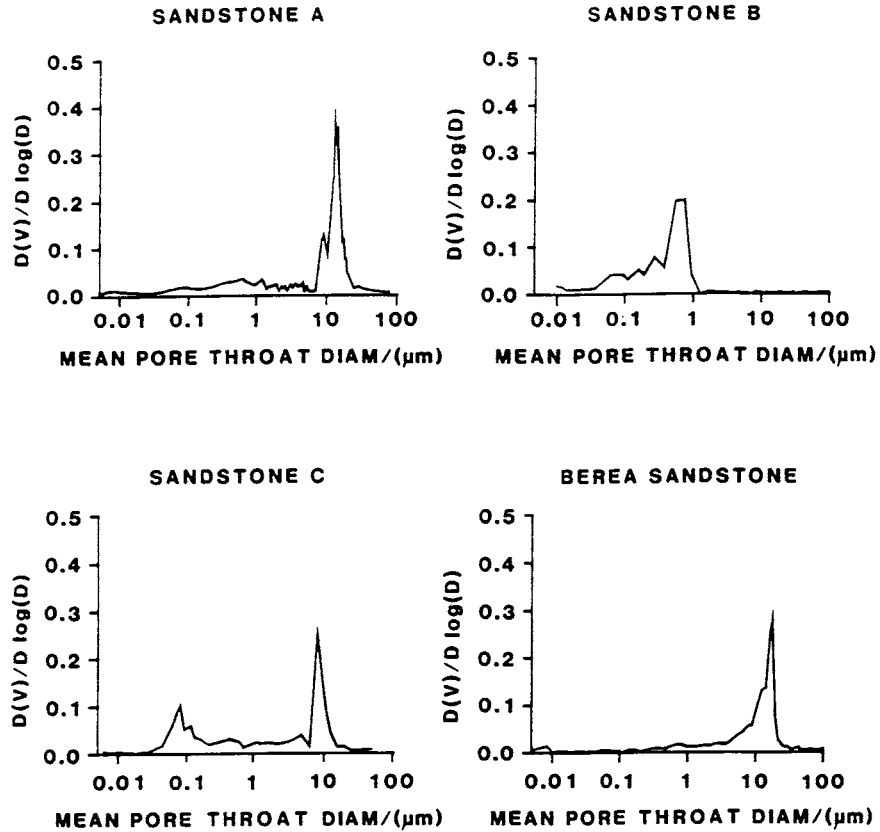


FIGURE 7 Pore size distribution.

TABLE 2 Krypton And Water Surface Areas.

Sandstone	Surface Area	
	krypton m^2/g	water m^2/g
A	3.0	3.7
B	3.1	4.4
C	4.6	4.8
Berea	1.1	1.8

The amounts of water evolved during TG/EWA from samples equilibrated at both 0.55 RVP and 0.9735 RVP are shown in Table 3. The data are expressed both in terms of water evolved as a percentage of total pore volume and as a ratio of the amounts evolved at 0.9735 RVP and 0.55 RVP.

TABLE 3 Water Evolved During TG/EWA.

Sandstone	Water Evolved		Ratio 0.9735 RVP / 0.55RVP
	@ 0.55 RVP % of PV	@ 0.9735 RVP % of PV	
A	1.5	7.1	4.7
B	2.4	18.5	7.7
C	2.3	22.6	9.8
Berea	1.1	6.0	5.5
Non-microporous materials	-	-	2.5 *

* taken from data shown in Figure 1

DISCUSSION

The mercury PSD profiles shown in Figure 7 illustrate the effect that different clay minerals have on the pore size distribution of reservoir sandstones. XRD analysis shows pore filling kaolinite as the major clay mineral present in Sandstone A and Berea sandstone. Both exhibit a unimodal PSD with pore size peaking just above $10\mu\text{m}$. Sandstone B, which contains almost exclusively pore bridging illite, exhibits a bimodal PSD with the larger pore size peaking just below $1\mu\text{m}$ and the smaller pores covering a range of sizes up to $0.5\mu\text{m}$. This is a truly microporous sample. Sandstone C contains mainly pore-lining chlorite with a lesser amount of illite. This material has a bimodal PSD, with the larger pore size peaking just below $10\mu\text{m}$ and the smaller pore size peaking just below $0.1\mu\text{m}$.

The krypton and water surface area values shown in Table 2 agree well, despite the fact that different molecules and different experimental techniques were used. As mentioned earlier, the adsorption of water onto the surface of rock minerals is extremely complex. However, the results do confirm qualitatively the premise that at 0.55 RVP, approximately two to three monolayers of water are adsorbed onto the rock mineral surfaces.

The amount of water evolved from samples equilibrated at 0.55 RVP is shown in Table 3, expressed as a percentage of total pore volume. "Bound" water constitutes only a very small percentage of the pore volume in all the rocks studied, i.e. between 1.1 and 2.4%.

Table 3 also shows the amount of water evolved from samples equilibrated at 0.9735 RVP. Equation 3 may be used to show that pores of up to $0.08\ \mu\text{m}$ diameter are filled with liquid water under these conditions. Sandstone A and Berea sandstone show the lowest values for "capillary" held water, filling 7.1% and 6.0% of total pore volume respectively. Sandstone B which contains almost exclusively illite has 18.5% of its pore volume filled and Sandstone C, which contains predominantly chlorite, gives the highest value at 22.6%.

The amounts of water evolved from samples equilibrated at 0.9735 RVP and 0.55 RVP, are expressed as a ratio in Table 3. For a rock with no microporosity this ratio is 2.5. Kaolinite bearing rocks sandstone A and Berea sandstone, have ratios of 4.7 and 5.5 respectively. Sandstone B, illite containing, has a ratio of 7.7 and sandstone C, chlorite containing, has a ratio of 9.8.

The ratio is used to compare the amounts of "capillary" and "bound" water under these specific relative vapour pressure conditions. For the reservoir rocks examined, the ratio increases according to the type of clay mineral that predominates, in the order kaolinite, illite and chlorite. However, these ratios are not dependent solely on the clay mineral type. They are also a function of many other parameters such as porosity, the amount of clay mineral present, its crystal size and distribution within the pore system. The highest ratio is obtained for the chlorite bearing sandstone C which shows an order of magnitude difference between the amounts of bound and capillary water.

CONCLUSIONS

Bound/capillary water relationships of reservoir rocks have been studied by the new technique of thermogravimetry/evolved water analysis TG/EWA. The rocks contain kaolinite, illite and chlorite, which are the clay minerals most commonly found in North Sea sandstones. It is especially significant that all the sandstones studied contain much more capillary water than bound water. The amounts held are strongly dependent on the type of clay mineral that predominates, along with its morphology and location within the pore space. In particular chlorite-containing reservoir rocks analysed in this study hold up to 10 times more capillary water than bound water. These results also dispel the myth that bound and capillary waters in reservoir sandstones are volumetrically equivalent.

ACKNOWLEDGEMENTS

The authors would like to thank D.B. Ryall and K.J. Streets for helpful discussions and the Sorption and Thermal Group for surface area and pore size distribution analysis. We also wish to thank BPX and BP Research for their support of this work and for permission to publish this paper.

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