Abstract

In this paper we describe a technique based on radio frequency plasma treatment in H₂O vapour to reproducibly clean and modify the surface energy of clastic and carbonate core material allowing the establishment of well defined wettability conditions. We present micro-tomographic observations of the pore-scale fluid distributions in strongly water wet clastic and carbonate cores. We then establish mixed-wet states in the same cores using controlled hydrophobation. Micro-tomography is again used to reveal the three-dimensional geometry and topology of water and oil wet regions. The tomographic data shows that under water wet conditions at intermediate saturations larger pores are predominantly oil filled while smaller pores remain water wet. We perform displacement experiments using clastic and carbonate cores at well defined wettability conditions and report measurements of resistivity index. These methodologies may provide insight into the role of rock microstructure and surface energy variability in determining recovery and production characteristics of oil and gas reservoirs.

Introduction

Wettability has a profound effect on reservoir recovery and productivity. Wettability controls fluid distribution and multiphase fluid displacement behavior. It can have a significant effect on original oil-in-place, reservoir performance, ultimate oil recovery and accordingly field economics. However, wettability is very difficult to measure and characterize. Commonly used measures such as Amott-Harvey and USBM characterize the rock fluid system via a “wettability index” (WI). WI ranges from -1.0, strongly oil wet, to +1.0 for a strongly water wet system. Systems within the range -0.3>WI>0.3 are referred to as “mixed wet” (Cuiec, 1991). In early studies of the effect of wettability on immiscible displacement, results were obtained for very strongly water wet and very strongly oil wet conditions under the assumption that the results will span all possibilities between these two conditions. It is now recognized that an infinite number of possible wetting states exists between these two extremes and the multiphase flow properties can exhibit a rich variety of behaviors (Morrow & Mason, 2001). WI only provides a single global average index and is therefore often unable to account for differences in multiphase transport properties for different rock types with similar indices. A fundamental understanding of wettability and its effect on recovery requires knowledge of the pore-scale distribution of fluids and an understanding of the complex interaction between the geometry and topology of the pore-space, the wetting preferences of the solid and the connectivity of different regions of wettability within the pore-space. Global average wettability indices cannot provide this information and little is currently known of the distribution and connectivity of fluids in real reservoir rocks particularly those of mixed wettability.

Because of the complex composition of crude oils (e.g., presence of asphaltenes, brine pH and salinity), rock surfaces (different mineral compositions) and colloid interactions, precise understanding of the variables controlling wettability in a reservoir are difficult to achieve. A better understanding of the role of wettability on recovery and production characteristics requires the development and study of rock-fluid systems having well defined wettability states. Model mixed wet systems have been generated with fractional wetted bead packs to help better understand the properties of mixed wet systems. Morgan & Pirson, 1964 varied the proportion of oil-wet and water-wet beads in a pack by treating a portion of the beads with a silane solution to render them oil wet. The remaining beads were untreated and water wet. By varying the proportion of beads idealized core material of different wettability states were generated. The goal of this paper is to describe a technique which can establish controlled mixed (fractional) wet states in reservoir core material.
In this paper we describe a technique to reproducibly clean and modify the surface energy of clastic and carbonate core material allowing the establishment of well defined wettability conditions. Taking simple hydrocarbon-free representatives of a carbonate and siliclastic we firstly apply a plasma cleaning process that produces a strongly water wet core. Strongly oil wet clastics are produced by surface grafting long hydrocarbon chains via silane coupling. In the case of carbonates, steric acid forms a strong ionic association with surface calcium ions to render these materials hydrophobic. Mixed wet conditions are established by partially saturating the strongly water wet core, rapidly freezing the core followed by flushing with a non-labile chemical group to render the exposed pore surface hydrophobic. The core is then thawed, drained and dried. The initial water saturation in the core determines the fraction of the pore space which remains water-wet and different wettability states are established with different initial water saturations. The pore-scale distribution of the wetting and non-wetting fluids in the core is imaged in three-dimensions using microtomography. The tomographic data shows that for mixed water-wet conditions at intermediate saturations larger pores are predominantly oil filled while smaller pores remain water wet. The observations are consistent with the pore-level conceptual model for fluid distribution and wettability alteration proposed by Kovscek et al, 1993 which forms the basis for incorporating wettability effects in network models. The technique to reproducibly clean and modify the surface energy of clastic and carbonate core material allows one to establish different oil/water and mixed wet states in the same core material. In the final section of this paper we give examples of drainage capillary pressure and resistivity index measurements in the same clastic and carbonate core material under different wetting conditions. The methods described in this paper—experiments on the same core material under controlled wettability conditions, coupled with 3D image-based study of the rock and fluid distributions—will help in understanding the complex multiphase transport properties in real reservoir core.

**Cleaning and Modifying Clastic and Carbonate Cores**

Cleaning processes begin with a regime of solvent washing in order to remove the bulk of the organics. However, flushing the core repeatedly with organic solvents does not guarantee that all contaminants will be removed and in all cases a thin film or monolayer will be left behind. Further, the act of solvent extraction certainly redistributes contaminant onto uncontaminated surfaces. For example, Hirasaki et al, 1990 showed that traditional cleaning methods like the Dean-Stark extraction method does not achieve water-wet conditions in cores that were initially not water wet. The method also changed cores that were water wet initially into ones that were less water wet than before. However, a critical step in any solvent cleaning procedure is the drying of the core and again this acts to redistribute contaminants (Zhang et al., 2006). Ultimately, it is unlikely that these methods will remove monolayers entirely, if at all. As a monolayer alone is sufficient to change a water-wet surface to oil-wet one it is crucial that any cleaning process is rigorous and complete. Chemical treatments that oxidize or cleave these monolayers offer insufficient control to avoid damaging the core material; examples of damage include the etching, roughening or removal of core minerals.

We have used a vacuum process, a cold electric plasma of water vapour, to physically remove monolayers and thin organic films. Our plasma apparatus consists of a cylindrical glass vacuum chamber with an external antenna wrapped in a single loop around the mid-section. The stainless steel ends are earthed. A balanced load at 135 kHz and 100 W forward power is transmitted through a pressure of between 0.1 to 0.2 torr water vapour for 3-5 min. The system is continuously pumped during the exposure. Within the water plasma highly reactive radical species and ions such as H*, H+, OH·, OH*, O* and O+ react with the surface. It is surprising to us that these short lived plasma species penetrate so far into the tight pore space of a rock. Most materials become highly hydroxylated which greatly increases their affinity with water. The efficiency of cleaning is determined by the nature of the reactive species and their partial pressure both of which are a complex consequence of rf power and total pressure. The energy of the plasma treatment means that no sputtering is likely and mass spectral analysis shows that only very light molecular fragments such as CO are liberated from an organically contaminated surface. In this way molecularly thin films are lyzed and evaporate as gaseous molecules. Macroscopic thick films greater than several hundred nanometres are not removed; they are however rendered hydrophilic. The permanency of the hydrophilicity of these thick films depends very much on the nature of the material and is difficult to state without testing. It is certain however that thick organic films do revert to their native lower energy state within a short time (days to weeks). Figure 1 illustrates this effect on paraffin, a solid substrate with a contact angle with water >100°. After plasma treatment the surface hydroxyl groups relax back into the paraffin within a few days, in order to minimize the surface energy. Samples kept immersed in water after treatment remain water wet for many months as the association of the surface hydroxyls with the water prevents the surface relaxation seen in the dry state.

To illustrate the reproducibility of the plasma and hydrophobing processes non-porous silica and calcite flats were plasma treated, made hydrophobic and then plasma re-treated. For calcite 10⁻³M steric acid in heptane and for silica 10⁻³M octadecyltrichlorosilane in heptane were found to render the surfaces hydrophobic by the chemical grafting of a monolayer. Figure 1 shows the results using the contact angle a water droplet makes on the two substrates after varying treatments. This proves only that the surface energy can be recovered and according to Senden and Ducker (1992), who employed Atomic Force Microscopy, show no appreciable increase in surface roughness.
**Figure 1:** A sequence of contact angles with water on substrates firstly plasma treated, hydrophobed with a surface agent, tested again after 24 hr and finally re-plasma treated. Silica is shown as circles. Blue circles denote silica hydrophobed with the silane, open circles silica hydrophobed with steric acid. Close circles show the controls in which no silane was used. Diamonds show results for calcite: open diamonds treated with steric acid, closed diamonds treated with silane. The X’s are for paraffin, which was not exposed to a hydrophobing agent and was tested after 36 h; reversion to the native low energy state is observed. The images on the right-hand margin show examples of images used in determining the contact angle.

In comparison with a flat substrate the increased degrees of freedom a porous substrate offers requires that water films are demonstrated after plasma treatment. Figure 2 shows a partially saturated plasma treated core of Fontainebleau sandstone rapidly frozen in nitrogen slush, fractured and cryogenically imaged in an SEM. Note that although the degree of saturation was low, < 20%, films are clearly present in regions of high curvature. Micro-tomography does not have the resolution to show film structure at this length-scale however it compliments cryo-SEM by providing valuable 3D distributions.

Figures 3 and 4 compare endpoints of spontaneous imbibition processes on core material “as received” in our laboratory and samples which have been plasma treated; the results illustrate both the ability of plasma to clean core and to produce conditions of uniform wettability. Figure 3(a) shows a sample of clean water-wet sand after imbibition; in this case the imbibition proceeded slowly so as to limit the degree of trapping. In comparison plasma treatment rendered this clastic strongly wetting; rapid imbibition was observed, resulting in a high degree of air trapping. Note the uniformity of the trapped phase showing a homogeneous surface energy. Figure 4 illustrates the vast difference in imbibition into a core with a heterogeneous compared with a homogeneous surface energy. Figure 4(a) shows a mono-mineralic dolomite core; the wetting phase distribution point to a distribution of surface energies as a consequence of solvent flushing. Figure 4(b) shows the same core after cleaning; one now observes a uniform distribution of trapped air, without any noticeable boundary effects.

**Figure 2:** A cryo-SEM of the frozen water films seen here by labelling with 1M CsI. The left-hand image shows a fracture through Fontainebleau, the right-hand a carbonate.
Figure 3: Longitudinal mid-sections and cross-sections through 5mm cores of Fontainbleau sandstone after spontaneous imbibition of 1M CsI solution for ‘as received’, (a), and after plasma treatment (b).

Figure 4: Longitudinal mid-sections and cross-sections through 5mm cores of a carbonate after spontaneous imbibition of 1M CsI solution for ‘as received’, (a), and after plasma treatment (b).

As a further illustration of the effective penetration of the plasma into the pore space we treated a microporous chalk and followed the imbibition of 1M aqueous CsI solution using time resolved radiography. Figure 5(a) shows a radiograph of a 1mm thick slab of chalk within a hermetically sealed container. The slab sits in contact with a dry glass sinter and filter paper to give a good capillary bridge. Slowly a vessel of the CsI solution is raised until it touches the bottom of the sinter. Spontaneously the solution conducts through sinter, paper and into the slab. At this point a time series of radiographs is recorded and later normalised by the dry image. In this way the passage of CsI was recorded for the ‘as-received’ and plasma treated chalk. Figure 5(b) shows a time plot for imbibition process. Not only does the rate increase but also the degree of saturation for the plasma treated chalk over the untreated material. The chief conclusion is that the chalk becomes much more highly wetting and saturates to a degree more that 2 ½ times the ‘as received’ material. Clearly the spatial resolution of technique is insufficient to state anything about the patchiness of the fluid distribution.

Figure 5: a) a radiograph of a 1M CsI saturated 20mm wide, 2mm thick slab of chalk. The dashed areas delineate regions used in the radiograph to relate each frame in the time sequence to each other. The dark ragion at the bottom is a sinter which acts to couple the solution to the slab. b) a plot of the imbibition rate for ‘as received’ chalk (crosses) and the same slab after plasma treatment (triangles).

Generating Mixed Wet Cores
The cryo-SEM gives a clue to the process used to make mixed wetting cores. The uniform distribution of water in a strongly water-wet core can be used a template for both the water-wet and oil-wet surfaces within the pore-space. The first step in generating a mixed wet core is to under-saturate a water-wet core with water. Ideally this distribution of the water phase is limited to water films and small pores. Adding a reactive hydrophobic agent to this partially-saturated core would lead to the exposed surfaces becoming hydrophobic. The chief difficulty with using an initial water saturation to define the distribution of water-wet regions comes with the addition of a reactive hydrophobing agent. If the water phase is mobile the hydrophobing agent readily pushes the water around. This movement of water generally leads to a heterogeneous distribution of water and oil wet regions and in many cases the water phase is observed to have moved to one extremity of the core. This is very clearly seen from pore scale micro-CT imaging data (Figure 6).
The problem is resolved by immobilizing the water by rapidly freezing the core. By immersing in the respective hydrophobing solution kept below 0°C the water films remain immobile while the exposed surface becomes oil-wet. The mixed–wet cores are then drained and flushed of residual hydrophobic agent while the water films remain frozen. The oven dried core (110°C) is then ready for flooding experiments and measurements via micro-tomography or conventional core analysis.

3D Imaging of Phase Distributions:

As already shown in Figs. 3, 4 and 6, the pore-scale distribution of the wetting and non-wetting fluids in the core can be imaged in three-dimensions using microtomography. The ability to establish different oil/water and mixed wet states in the same core material coupled with 3D tomographic imaging of the fluid phase distribution under these different conditions allows one directly measure the fluid phase distributions and connectivity of fluids in real reservoir rocks under different wettability conditions. In this section we briefly describe some of the methods used to extract this fluid phase distributions in 3D from microtomography. The example is based on experiments of a water wet carbonate core.

Three dimensional scans of a carbonate core (sucrosic dolomite) were obtained for the dry core material and after a spontaneous imbibition experiment on the strongly water wet core (Fig. 7(a)-(b)). Phase separation of the pore phase from the solid phase in the dry image (a) led to an estimated porosity of 25.7%. The dry sample was then removed, treated to strongly water wet and saturated with the CsI solution, and reimaged (Fig. 7(b)). The two samples are aligned in three dimensions using image registration techniques. The registration technique is based on an optimal superposition of two 3D images (Latham et al, 2008) and allows one to obtain voxel scale alignment of the wet and dry images with high fidelity. Fig. 7(c) shows the superposition of the two aligned images in three dimensions. The estimated residual non-wetting fluid saturation is $S_{nw}=17\%$.

The connectivity of the pore phase can also be visualized in 3D using a pore network partitioning. In Fig. 7 (d) we show a subset of the pore throat network for the dry sample; the image volume contains 25530 pore bodies, 61903 pore throats and an average connectivity of 4.8. Other geometric and topological parameters can be determined from the resultant network including pore and throat size distributions and pore to throat aspect ratios. On superposition of the image after water imbibition on the pore network partition one can examine the fluid occupation within individual pores. One can also define the fluid saturation states in all pores within the image volume. In Fig. 7 (e-f) we quantify the water saturation as a function of individual pore volume. Conventional wisdom would argue that the smaller pores would exhibit the highest wetting phase saturations while the larger pores would exhibit higher non-wetting phase saturations. This is observed in Fig. 7 (f) where the red line shows the running average of non-wetting phase saturation as a function of pore body size; the non-wetting phase is concentrated in the largest pores. The observations are consistent with the pore-level conceptual model for fluid distribution and wettability alteration proposed by Kovscek et al., 1993 which forms the basis for incorporating wettability effects in network models.
Figure 7: (a) Single 2D slice from tomographic image of dry sample; (b) slice from image of wet sample; (c) slice from 3-phase segmentation showing void (orange), wetting phase (blue) and solid (black); (d) Pore-throat network extracted from full pore space in (c); (e) Fluid occupancy of crevices and pore bodies as defined by covering radius map; (f) fluid occupancy of pore bodies as defined by pore-throat network; scatter plot shows local saturations for all 60,000+ pores; the red line gives the running average water saturation as a function of pore volume.
While only illustrated here for a single sample, the ability to optimally register the same image volume multiple times leads to an exciting opportunity to image the same core material under different wetting scenarios, after different flooding conditions with different fluids and at different saturations. This method, coupled with the ability to generate controlled mixed wet conditions in cores will provide improved understanding of pore scale mechanisms driving oil and gas displacement and implications of wettability to recovery.

**Varying Wettability in Identical Core Material: Measurement of Resistivity Index**

Morgan & Pirson, 1964 examined the effects of mixed or fractional wettability on resistivity measurements. They treated a portion of strongly water-wet beads with an organochlorosilane solution to render them oil wet. Resistivity measurements were made for packs containing varying proportions (0% to 100%) of oil-wet and water-wet beads. The Archie saturation exponent ranged from 2.5 to 25. This is one of many studies showing that wettability has a strong effect on resistivity exponents (see also e.g., Sweeney & Jennings, 1960; Man & Jing, 2002, Fleury et al., 2004). In the present study we establish different oil/water and mixed wet states in core material and perform resistivity measurements. We give examples of drainage capillary pressure and resistivity index measurements for one clastic and one carbonate core plug under different wetting conditions. Plugs of approximately 2.5cm in diameter by 2.5cm in length cut from an outcrop sandstone (Fontainebleau) and a reservoir carbonate (bioclastic pack/grainstone) were used in the experiments. The cores were conditioned to water, mixed and oil wet conditions using the procedures described in the previous section.

**Drainage Capillary Pressure and Resistivity Index Measurements.** Drainage capillary pressure and resistivity index were measured using the porous plate technique. The porous plate experiments were performed using the MK4 modular equipment purchased from ErgoTech, UK. The apparatus works based on the 4-electrode method for resistivity measurements. The cores were first saturated with 2 wt% NaCl brine after evacuation for 12 hours. The cores were then placed in the apparatus and the reference resistivity index was measured at zero capillary pressure. The pressure was then increased by injecting a brine-saturated N\textsubscript{2} to a constant value and the displacement of brine by gas was observed in a precise graduated cylinder until no more changes in produced volume and resistivity measurements were observed. The injection pressure was then increased to the next level and the same procedure was followed and the full drainage curves of capillary pressure and resistivity index were obtained. The maximum injection pressure was 10 bars, which was the threshold pressure of the porous plate. All the tests were performed at ambient conditions, 22°C.

**Experimental Results**

**Fontainebleau Sandstone:** Under water wet conditions at intermediate and high water saturations, \( S_w > 0.2 \), we observe classic Archie behaviour, \( n = 2 \) (Fig. 8(b)). The experimental results for the stabilized resistivity index at lower brine saturations exhibit a deviation from the Archie behaviour with the value of \( n \) decreasing dramatically. We believe this deviation from \( n = 2 \) is due to the presence of continuous water films at submicron length scales [Knackstedt et al., SCA 2007, Kumar, unpublished]. We also measure RI under mixed wet conditions (design of 50% PV water wet, 50% PV oil wet) and observe \( n \sim 3 \) for intermediate saturations and lower values of \( n \) at lower saturations.

**Bioclastic Reservoir Carbonate:** In the first RI experiment the measurement was undertaken on the sample as originally received at the laboratory. The “as received” core was in a mixed wet state with an Amott Index = 0.3. The experimental data for this core exhibited classical Archie behaviour with \( n=2 \) (Fig. 9(b)). The core was then cleaned to strongly water wet and the experiment repeated; in this case the core exhibited non-classical behaviour with \( n<2 \) and a jump to \( n=2 \) for \( S_w<0.2 \). Capillary pressure data for the core shows that a significant fraction of the porosity is microporous. The low values of \( n \) may be associated with enhanced connectivity of the water saturated microporous phase. Oil wet results (data not shown) exhibits values of \( n \) larger than 2.5 for high to intermediate saturations.

Similar, non standard, behaviour for the resistivity of carbonates has been widely reported (see e.g., Fleury et al., 2004). Petrophysicists suspect that the major cause for this behavior is rock heterogeneity, the complexities of pore structure in complex lithologies and the underlying wettability distributions. The continued development of an integrated experimental and 3D image-based pore scale study of the rock microstructure and fluid distribution coupled with displacement experiments under controlled wettability conditions will help in understanding the apparently anomalous resistivity behaviour in these complex lithologies.
Fig. 8: (a) Drainage capillary pressure and (b) RI measurements for Water wet and mixed wet Fontainebleau core. The variation due to the introduction of the mixed wetting condition leads to values of the saturation exponent $n$ larger than 2. For the water wet core we observe classical Archie behavior for $S_w > 0.2$ and value of $n$ decreasing dramatically for $S_w < 0.2$.

Fig. 9: (a) Drainage capillary pressure and (b) RI measurements for carbonate core material under three different wettability conditions. In the “original” experiment the core originally received at the laboratory was measured. The core material was in a mixed wet state with an Amott Index = 0.3 and classical Archie behavior is observed. The core was then cleaned to strongly water wet and the experiment repeated; the saturation exponent is now strongly dependent on saturation.

Conclusions
Based on the present study, the following conclusions may be drawn:

1. Plasma cleaning renders carbonate and siliclastic core plugs strongly water-wet. Hydrophobic conditions in clastics are produced by silanation and in carbonates via steric acid. Mixed wet cores are established by partially saturating the strongly water wet core, rapidly freezing the core followed by flushing with a non-labile chemical group to render the exposed pore surface hydrophobic. The core is then thawed, drained and dried. The wettability states are reproducible.

2. Tomographic imaging can be used to determine fluid saturations in individual pores in partially saturated cores. In a strongly water-wet core we observe, in accordance with conventional wisdom, that larger pores are predominantly filled with non-wetting fluid while smaller pores are saturated with the wetting fluid.

3. Variations in wettability can produce dramatic differences in resistivity.

4. Experiments on the same core material under controlled wettability conditions, coupled with 3D image-based study of the rock and fluid distributions, will help in understanding observed anomalous resistivity and multiphase flow behaviour in real reservoir core with complex lithologies.
Nomenclature
\( n \) Archie’s saturation exponent
\( PV \) pore volume
\( S_w \) wetting-phase saturation
\( WI \) Amott wettability index
\( \phi \) porosity

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