CAPILLARY PRESSURE AND PORE SIZE DISTRIBUTION FROM WATER INJECTION: A FEASIBILITY STUDY

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ABSTRACT

MICP (Mercury Injection Capillary Pressure) is a standard procedure for core analysis. However, the use of mercury is forbidden in some environments and so far there are no alternative methods. NMR provides information on pore distribution but is not directly related to the capillary pressure.

This paper presents a feasibility study for replacing mercury by water or brine (BICP: Brine Injection Capillary Pressure). The principle is to change the wettability of the rock in order to have a surface not wetted by water in the presence of air.

We present experimental results realized with a siliconate treatment that has the advantage to be safe and water soluble (no solvent). The samples are 100% saturated with a siliconate solution and then dried. This treatment phase is also used to determine the porosity of the sample from the difference of mass before and after drying (assuming a known grain density).

The experiment is conducted similar to mercury injection in a penetrometer with brine instead of mercury. Initially, the sample is not evacuated under vacuum and air compressibility is taken into account in the interpretation. So far, the pressure is limited to 30 bars, but there is no technical limitation. Cycles of injection/withdrawal are also performed like for mercury.

The first important result is that the spontaneous imbibition when the treated sample is put into brine is limited to around 10% of the pore volume. The second point is that we are able to build capillary pressure curves, with volume stabilization at each step, in both injection and withdrawal. Results on samples with a wide range of permeabilities show a qualitative agreement with results obtained with mercury injection.

In conclusion, we do not claim the same accuracy as with mercury but the method can be useful for safe and quick rock-typing measurements.

INTRODUCTION

MICP (Mercury Injection Capillary Pressure) is a standard procedure for core analysis.

The advantage of mercury is that it is a non-wetting fluid for any type of surface and that the contact angle does not depend on the nature of the surface. However, the use of mercury is forbidden in some environments and so far no alternative methods are available. NMR provides information on pore distribution but is not directly related to the capillary pressure.

This paper presents a feasibility study for replacing mercury by brine (a method that we call BICP: Brine Injection Capillary Pressure). The principle is to change the wettability of the rock in order to have a surface not wetted by water in the presence of air. Such chemical treatments are used in the domain of civil engineering to prevent humidity in stones (siliconates), to study the structure of catalysts (silane), or in well treatments to prevent water blocking (see the review by Anderson [1]).
For gas condensates, Tang and Firoozabadi [2] have increased the mobility of the liquid phase by using chemical treatments with fluoropolymers (FC-722 and FC-759 manufactured by 3M Corporation). In their experiments, the rock becomes intermediate gas-wetting and the spontaneous imbibition is around 10% of pore volume after treatment on Berea sandstone.

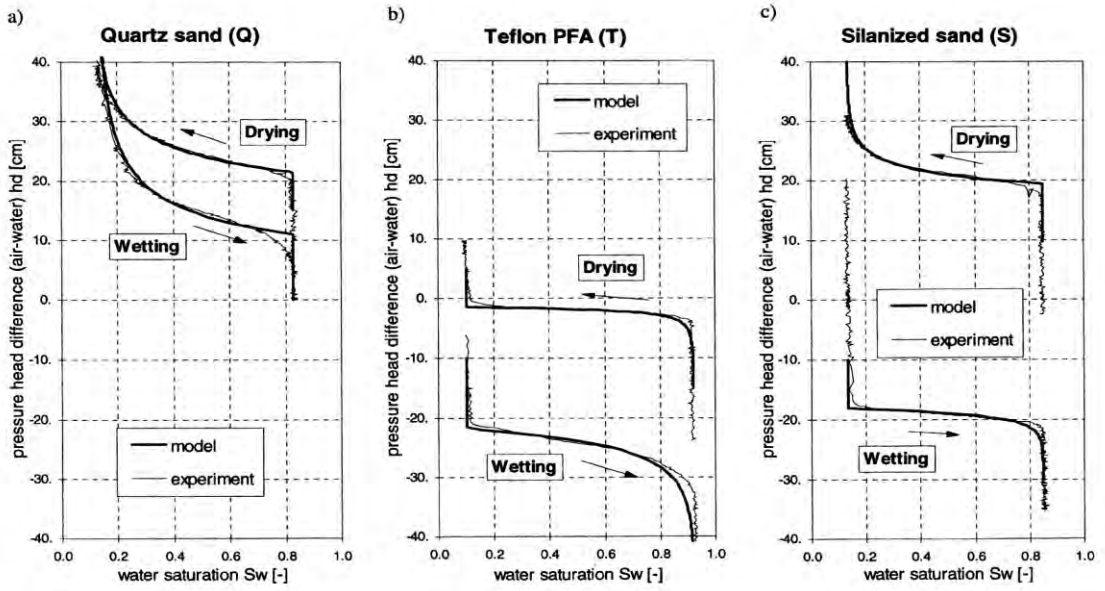

Figure 1 - Effect of silane treatment on air/water capillary pressure curves (after Ustohal et al. [5])

Silane treatment is currently used in laboratories to prevent water retention in glass burettes and pipettes. Historically, it was used in fluid mechanics laboratories to allow a flat meniscus in the glass tubes used to measure the pressure with the height of a water column. It consists in a strong treatment with a 50% mixture of nitric and sulfuric acids followed by soaking in a silane solution in boiling toluene. This treatment is currently used for the study of catalysts [3]. It has also been used to study the mixed wettability on pure quartz (Lombard [4]). However, the treatment is not suitable for real rocks (carbonate rock or cement are dissolved).
Ustohal et al. [5], have compared air/water capillary pressure curves obtained on silane treated and untreated quartz sand. In Figure 1, drying is equivalent to drainage (secondary) and wetting to imbibition, using the standard definitions used in core analysis (imbibition is an increase of water saturation). Pure quartz is water-wet (hydrophilic), with both imbibition and drainage curves being positive (Figure 1a). The Teflon (Figure 1b) is hydrophobic with both curves being negative. The treated quartz present symmetrical curves for imbibition and drainage, in agreement with a contact angle

around 90° observed after silane treatment (flat meniscus in a tube). We recall that a 90° contact angle leads to zero capillary pressure only in a straight capillary tube. In an angular pore, a displacement takes place with a curvature and consequently with a non-zero capillary pressure with magnitude similar in drainage and imbibition but with opposite sign (Figure 2).

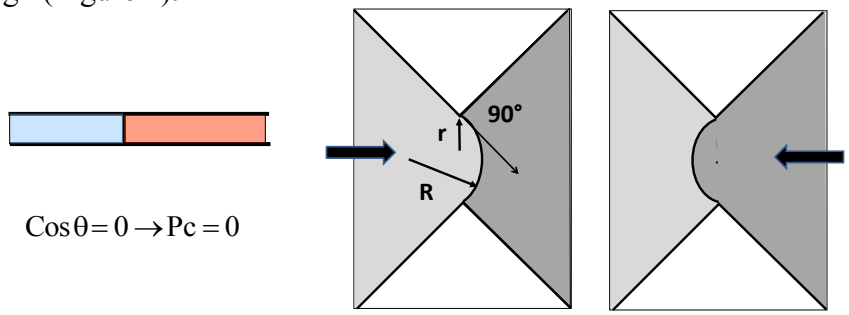

Figure 2 – Capillary pressure in a straight tube and in an angular pore for the case of 90° contact angle.

Instead of silane treatment, we have used a methyl siliconate of potassium (product T51 from Rhodia). This product is used in civil engineering for preventing humidity in the stone walls. It presents the advantages to be soluble in water and non-toxic. This product had also been tested for wettability treatment in the oil industry [6].

EXPERIMENTAL SET-UP AND PROCEDURE

Samples

We have used several samples, carbonates and sandstones, with a wide range of permeabilities and volumes of a few cc (around 4 grams of dry rock). For all the samples, the mercury injection has been performed.

Chemical treatment

Several concentrations have been used and so far, the optimum has not been determined. Several procedures for drying have been tested, either at atmospheric conditions or under CO2 atmosphere.

Experimental set-up

The experimental set-up is similar to a mercury porosimeter, except that we do not use vacuum. The sample is placed in a small chamber containing brine and it's the pressure is increased. The volume of water entering the sample under pressure is measured by a capacitance system, since brine is conductive. As for mercury, a blank measurement without sample is used for the correction of the cell compressibility. A correction is also applied for the effect of temperature on the volume of brine and capacitance measurement. The maximum pressure is 30 bar but it can be easily increased.

Procedure

The dry sample is 100% saturated with the siliconate solution using vacuum and pressure to dissolve the trapped air. The porosity is then derived from the difference of mass

between dry and saturated sample (assuming that the grain density is known). The sample is slowly dried at room temperature to let the siliconate polymerize on the rock surface. Then the sample is put in brine for spontaneous imbibition and saturation is derived from its mass. The sample is placed into the chamber of the porosimeter filled with brine and the air trapped around the sample is removed. Pressure on brine is increased continuously or by steps. At maximum pressure, the pressure is then decreased to perform the withdrawal.
At end of experiment, the sample is removed and weighed to determine the final saturation.

Interpretations
The brine saturation is derived from the volume of brine after pressure and temperature corrections. The gas volume is derived from the initial gas volume and brine saturation. The pressure in the compressed air inside the pores is calculated from gas volume using Boyles' law, assuming that all the gas remains connected. Using the standard definition in core analysis, the capillary pressure is negative (pressure in air minus pressure in water) like in the third curve Figure 1. However, for comparison with mercury curves and calculation of the pore size distribution, we will use the opposite positive Pc curve.
Similar to MICP, the pore size distribution is calculated as the logarithmic incremental dS/d(LogP), without any adjustment of surface tension (50 dyne/cm and contact angle 50°).

RESULTS AND DISCUSSION

First, we always observe a spontaneous imbibition between 10 and 20% of the pore volume, similar to the observations of Tang and Firoozabadi [2].

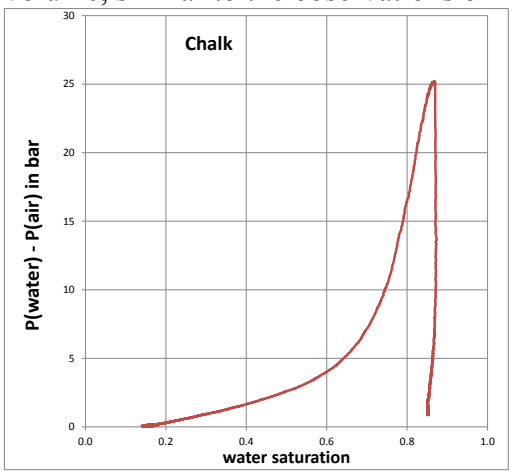

Figure 3: Pc curve for Chalk (around 5 mD). Water injection and withdrawal

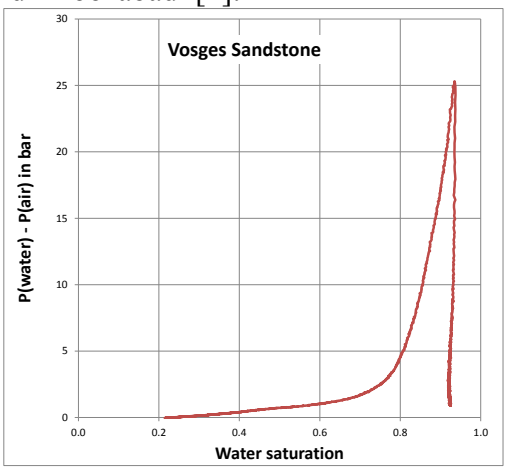

Figure 4: Pc curve for Vosges Sandstone (around 200 mD). Water injection and withdrawal

The main point is that we can build injection and withdrawal curve, like for mercury, pressure levels in agreement with permeabilities, i.e. higher pressures for lower permeabilities (Figure 3 and 4).

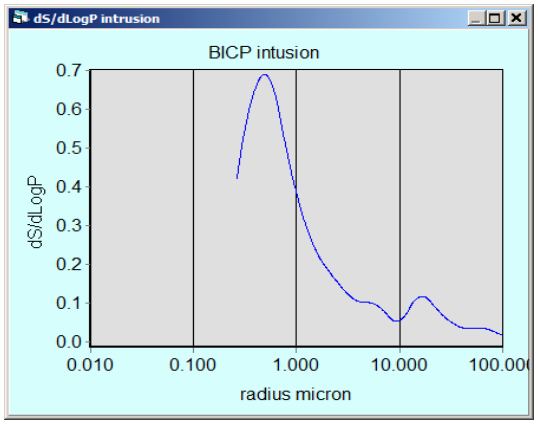

Figure 5 Tavel: psd from brine injection

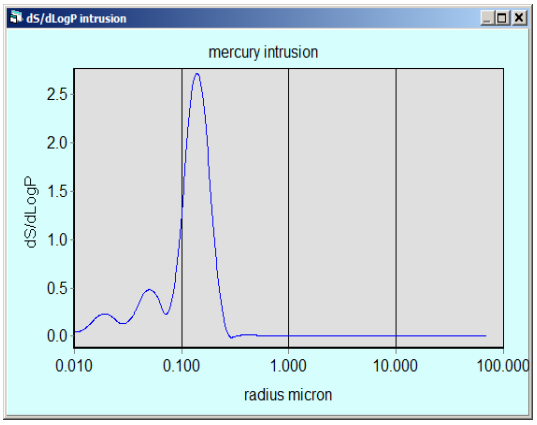

Figure 6 Tavel: psd from Hg injection

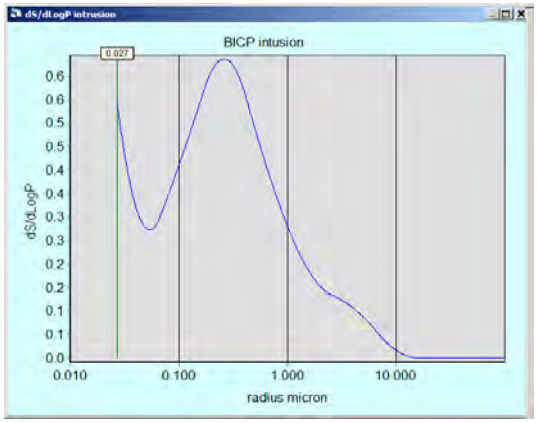

Figure 7 Chalk: psd from brine injection

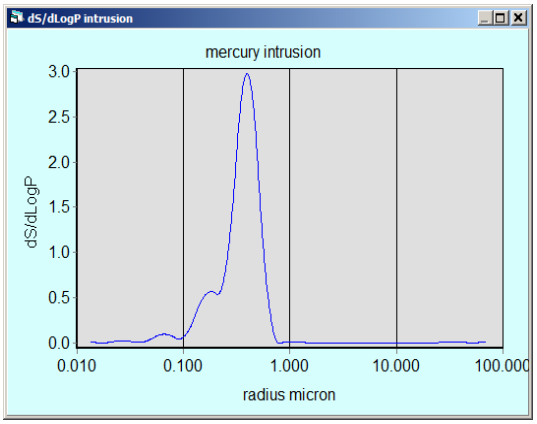

Figure 8 Chalk: psd from Hg injection

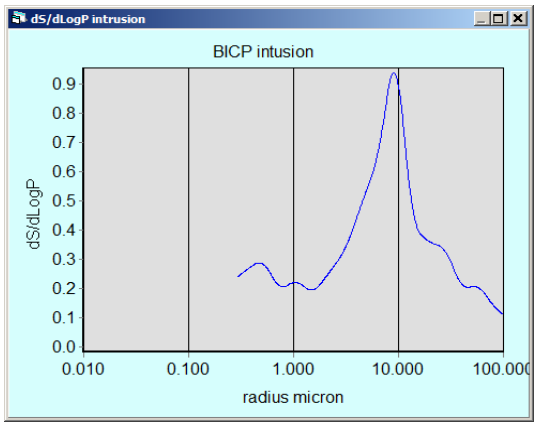

Figure 9 Vosges sandstone: psd from brine

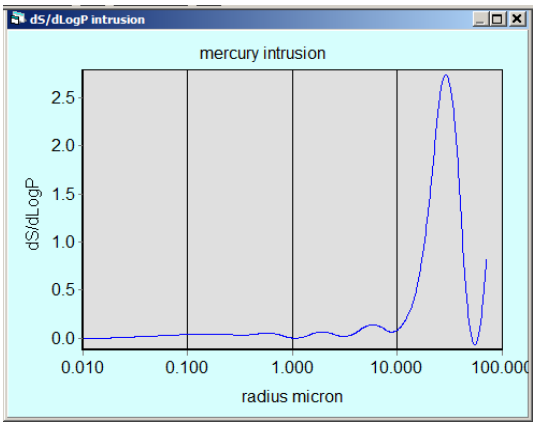

Figure 10 Vosges sandstone: psd from Hg injection

The pore size distributions are qualitatively in agreement with results obtained with mercury: small pores for Tavel and chalk samples (Figures 5 to 8) and large pores for Vosges Sandstone (Figures 9 and 10).

If we assume that mercury can be used as the reference, the agreement is not perfect, the pics are not exactly similar and the distributions are wider for BICP. Improvements are under investigations:

- Optimization of the siliconate concentration and the procedure for drying the siliconate solution (with or without CO2).
- Interpretation improvement: use of a different pressure correction for injection and withdrawal (hysteresis), use of the measured saturations to constrain the interpretation.
- Effect of injection speed; multistep injection with a better control of the equilibrium at each step.
- Use of initial partial vacuum or higher final pressure to minimize the uncertainty on final saturation

In addition, we will try to develop collaborations to use pore network simulators to study the effect of contact angle on pore size distribution.

CONCLUSION

The first important result is that the spontaneous imbibition when the treated sample is put into brine is limited to around 10% of the pore volume.

The second point is that we are able to build capillary pressure curves, with volume stabilization at each step, in both injection and withdrawal.

Results on samples with a wide range of permeabilities show a qualitative agreement with results obtained with mercury injection.

In conclusion, we do not claim the same accuracy as with mercury but with some improvements, the method could be useful for safe and quick rock-typing measurements.

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