

A MODEL FOR WETTABILITY CHANGE IN RESERVOIR ROCK

A. Hiorth and G. Virnovsky, RF-Rogaland Research

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Abu Dhabi, UAE, 5-9 October, 2004

ABSTRACT

We have developed a model describing wettability change in reservoir rock after primary drainage. Wettability change is dependent on phenomena at several length scales: macroscopic parameters like drainage pressure and ageing time, and small scale interactions like molecular interactions between brine, rock and oil. The model for ageing involves three parameters, ageing time, drainage pressure and a characteristic pressure. The characteristic pressure reflects the wetting film properties; it depends on chemical properties of the oil, water and rock and is related to the disjoining pressure.

The model has been used to describe wettability change in a bundle-of-tubes model. Pore-size distributions have been obtained for 5 different cores from the North Sea. The ageing model describes qualitatively the wettability change observed in experiments. Using experimental values for drainage pressure and ageing time we have found Amott-Harvey indices comparable with experimental values.

It is found that a wettability change, qualitatively described by the Amott-Harvey index, can be obtained for a single core for different ageing time and drainage pressure.

INTRODUCTION

Pore scale modelling has been successful to relate distribution of fluids in the pore space to macroscopic flow properties, such as electrical properties and permeability^[3, 11, 13, 16, 20, 18]. The paper by Blunt et al.^[3], together with the references therein, give a nice introduction to pore network modelling. In this paper we mainly focus on drainage and ageing. Drainage is the process where oil enters a porous media which is completely water filled and considered to be completely water wet. As the pressure in the oil phase is increased, more and more water is replaced by oil and when a maximum drainage pressure in the oil phase is reached the porous media is left for ageing. During ageing the oil may come in contact with the rock and change the wettability properties of the rock. The picture of wettability change we will adopt is the one described by Kovscek et al.^[15, 14]. Kovscek et al. describe wettability change in star shaped pores, where the centre of the pore becomes oil wet, and the corners stay water wet. This conversion from oil wet to water wet is dependent on the pressure in a thick water film close to rock, which will be explained in some detail

in the next section. Wettability change is also dependent of ageing time which has been confirmed by many experiments^[4,5,6,10,17,19].

PRIMARY DRAINAGE AND AGEING

Initially, the porous medium is considered to be completely water-wet and water filled. Completely water-wet in this context means that the oil-water contact angle is zero. Oil is injected in the porous media and will gradually expel water from the media as the pressure in the oil phase is increased. For a given capillary pressure, the Young-Laplace equation holds:

$$p_c = p_{oil} - p_{water} = \sigma_{ow} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1)$$

r_1 and r_2 are the main curvature radii of the interface. This process is referred to as primary drainage. When a maximum pressure in the oil phase is reached primary drainage ends. The maximum pressure is determined by the height above oil-water contact in the reservoir :

$$p_{drain} = p_c = (\rho_{water} - \rho_{oil}) g h, \quad (2)$$

Where ρ is the density of oil or water, g is the acceleration of gravity and h the height above oil-water contact. When oil enters a pore there will be a thick film of water between the oil and rock, which prevents active components in the oil to be adsorbed on the rock. The collapse of this water film is believed to be a necessary condition for adsorption of heavy components from the oil[14, 15]. As a consequence of this, the surface energy between oil-surface and water-surface will change. This change in energy is related to the surface tension and according to Young-Dupre's equation to the contact angle:

$$\sigma_{os} - \sigma_{ws} = \sigma_{ow} \cos \theta \quad (3)$$

Hence, after primary drainage the contact angle will be different from zero. A schematic illustration of what happens in a single pore is shown in **Figure 3**.

A MODEL FOR DRAINAGE AND AGEING

Collapse of Films and Disjoining Pressure

The disjoining pressure^[7, 8, 22, 12] is the pressure in a thin wetting film separating a non wetting phase and the rock. How the disjoining pressure behaves as a function of film thickness, temperature and chemical properties of oil, brine and rock will influence wettability alteration. The water film separating the oil-phase and rock may collapse into a thin film (~ one monolayer) dependent on the disjoining pressure. As already stated, the collapse of this film is believed to be a necessary condition for adsorption of active components from the crude oil and hence wettability alteration^[14].

Wettability Change after Ageing

After primary drainage the oil has entered a certain part of the pore-space. If the drainage pressure exceeds the metastable maximum of the disjoining pressure, p_c^{char} , the water film separating the oil from the rock may collapse and there is a possibility for wettability change.

The fraction of water-wet pores after a time t will be $n_w(t)$, if the porous media is completely water wet before primary drainage then $n_w(0) = 1$. If oil enters a pore and the drainage pressure is larger than the characteristic pressure determined from the disjoining pressure curve, that is $p_{drain}(t) - p_c(r^*) - p_c^{char} > 0$, there is a probability for wettability change. $p_c(r^*)$ is the entry capillary pressure for a pore with associated radius r^* . Number of films collapsing in a small time interval Δt are:

$$\Delta n_w(t) = -\tau (p_{drain}(t) - p_c(r^*) - p_c^{char}) n_w(t) \Delta t \quad (4)$$

Equation (4) can easily be integrated and we find

$$n_w(T_{drain}, p_{drain}, r^*) = \exp \left\{ -\tau \int_0^{T_{drain}} (p_{drain}(t) - p_c(r^*) - p_c^{char}) dt \right\} \quad (5)$$

Where T_{drain} is the drainage time. Note, that the drainage time includes both the time of the drainage process, and the ageing time, after the drainage process has been completed. In the lab, this drainage time will be of the order of weeks and in the reservoir it will be infinite. If we assume that the drainage pressure is increased to maximal value immediately, $p_{drain}(t) = p_{max}$ we find the following expression for decay of water-wet pores:

$$n_w(T_{drain}, p_{drain}, r^*) = \exp \left\{ -\tau (p_{drain}(t) - p_c(r^*) - p_c^{char}) T_{drain} \right\} \quad (6)$$

$$\tau T_{drain} = \frac{T_{max}}{p_{norm}}, p_{norm} = 50 \text{ kPa}$$

We have introduced a dimensionless drainage time, T_{max} .

The wettability change can be expressed using the concept of pore-size distribution as follows. The total pore size distribution density is $f(r)$, then after a drainage time T_{drain} it will split into the following two parts:

1. water-wet pores : $f_{ww}(r) = n_w(T_{max}, p_{drain}, r) f(r)$
2. oil-wet pores: $f_{ow}(r) = n_w(T_{max}, p_{drain}, r) (1 - f(r))$

The constant τ needs to be determined from experiment. This constant will in general be dependent of temperature, chemical properties of oil, water and rock. For oil containing no active components this constant must be zero as there will be no wettability change.

Model of Porous Media.

In order to compare the ageing model with experimental data we need a model for the porous media, for this purpose we will choose a bundle of circular tubes. The medium will then be characterized by a pore size distribution density, $f(r)$.

Drainage

We consider the porous medium to be completely water wet and water filled initially. The oil will then enter the largest pores first and the final the oil distribution in the medium will be determined by the drainage pressure. For a given drainage pressure (capillary pressure), p_{drain} , oil will enter all pores with $r > r^* = 2\sigma_{ow} / p_{drain}$, hence the oil saturation after drainage will be:

$$S_o = \frac{1}{V} \int_{r^*}^{\infty} \pi r^2 f(r) dr, V = \int_0^{\infty} \pi r^2 f(r) dr. \quad (7)$$

V is the total pore volume of the porous media. We can then rewrite equation (7):

$$S_o = 1 - \frac{1}{V} \int_0^{r^*} \pi r^2 f(r) dr = 1 - S_w \quad (8)$$

$$S_w = \frac{1}{V} \int_0^{r^*} \pi r^2 f(r) dr.$$

Ageing and Imbibition

After drainage, the presence of the oil in the porous media can change the wettability of the media. This process for a bundle of tubes model is schematically shown in **Figure 4**. Note that a single physical pore is represented by several cylindrical tubes. According to equation (6), a part of the pore space invaded by oil will be oil wet after ageing. In this paper we will assume it to be converted to completely oil wet, in a sense that a contact angle of 180° is prescribed to the oil-wet surface. During water imbibition, water will enter the water wet pores first (starting from the smallest), and then the oil-wet pores (starting from the largest).

During spontaneous imbibition for any given oil-water capillary pressure, $p_c > 0$, all oil-wet pores will be filled with oil as well as some of the large water-wet pores:

$$S_o = \frac{1}{V} \int_0^{\infty} \pi r^2 f_{ow}(r) dr + \frac{1}{V} \int_r^{\infty} \pi r^2 f_{ww}(r) dr \quad (9)$$

$$S_w = 1 - S_o = \frac{1}{V} \int_0^r \pi r^2 f_{ww}(r) dr$$

where $r = 2\sigma / p_c$.

At forced imbibition, for $p_c < 0$, all water-wet pores will be filled with water together with some of the large oil wet pores:

$$S_w = \frac{1}{V} \int_0^{\infty} \pi r^2 f_{ww}(r) dr + \frac{1}{V} \int_r^{\infty} \pi r^2 f_{ow}(r) dr = 1 - \frac{1}{V} \int_0^r \pi r^2 f_{ow}(r) dr \quad (10)$$

$$r = -2\sigma / p_c, \quad p_c < 0.$$

From equation (8), (9) and (10) we can calculate drainage and imbibition curve from a given pore size distribution, drainage pressure and ageing time.

THEORY VS. EXPERIMENT

We have compared our model with experimental drainage and imbibition curves taken from five different cores in the North Sea. Some physical properties of the five cores are shown in **Table 4**. In order to compare our model with experiments, we need to assume a functional form of the pore size distribution, we have chosen a linear combination (mixture) of two Weibull distributions:

$$f(r) = \sum_{i=1}^2 \omega_i f_i(r) = \sum_{i=1}^2 \omega_i \frac{\alpha_i}{\gamma_i} \left(\frac{r}{\alpha_i} \right)^{\gamma_i-1} \exp\left\{-(r/\alpha_i)^{\gamma_i}\right\} \quad (11)$$

$$\omega_1, \omega_2 > 0, \quad \omega_1 + \omega_2 = 1$$

This distribution contains five parameters which need to be determined, $\alpha_1, \alpha_2, \gamma_1, \gamma_2, \omega$. From equation (8) it is straight forward to calculate the drainage curve:

$$S_w = \sum_{i=1}^2 \frac{\omega_i \alpha_i^2 \Gamma(2/\gamma_i + 1) P(2/\gamma_i + 1, (2\sigma_{ow} \cos \theta / (p_c \alpha_i))^{\gamma_i})}{\alpha_1^2 \Gamma(2/\gamma_1 + 1) + \alpha_2^2 \Gamma(2/\gamma_2 + 1)} P(a, x) = \frac{1}{\Gamma(a)} \int_0^x e^{-t} t^{a-1} dt \quad (12)$$

Where $\Gamma(a)$ is the Gamma function and $P(a, x)$ is the incomplete Gamma function. Note that $\omega_1 = 1 - \omega_2 = \omega$. Equation (12) has been fitted to experimental drainage curves and the set of parameters obtained are shown in Table 1.

Core 1-3 are taken from the same field and has been aged for three weeks, for Core 1-3 T_{Max} has been chosen to mach the imbibition curve of Core 3. Cores 4 and 5 are from a different field and the ageing time has been chosen to match the imbibition curve of Core 4. For all cores we have chosen the characteristic pressure for the collapse of the thick water film to be zero. From the curves in **Figure 5** and **Figure 1**, we see that the predicted imbibition curve are somewhat higher than the experimental and network curves for $P_c > 0$.

There are a wide variety of wettability indices; we will use the Amott-Harvey index to quantify the wettability alteration in this model. In an experimental situation this index includes hysteresis, this model does not have any hysteresis. In this model Amott-Harvey index, I_A , is directly related to the intersection of the imbibition curve with the S_w -axis, S_w^* :

$$I_A = 2S_w^* - 1 \quad (13)$$

For Core 1-3 the Amott-Harvey index is given in Error! Reference source not found. for different ageing time together with the experimental value.

By varying both ageing time and drainage pressure we can obtain equal Amott-Harvey index, as shown in Error! Reference source not found..What happens is in fact that a larger part of the pore space gets invaded by oil as the drainage pressure increases and a larger volume is subjected to ageing, hence the ageing time must be shorter in order to obtain the same oil wet pore volume.

Lab and reservoir conditions

This model makes it possible to investigate what happens if ageing time and drainage pressure is varied. The two cases of interest are lab and reservoir conditions. In the lab one tries to mimic what happens in the reservoir, however in the lab one has a limited amount of time available. A short ageing time has then been exchanged with a correspondingly higher drainage pressure.

Ageing time in the reservoir is considered to be infinite. The drainage pressure or capillary pressure is determined by equation (2). The fraction of oil wet pores is then determined by the height above oil water contact, the density difference of oil and water and the size of the metastable maximum of the disjoining pressure (p_c^{char}). Clearly, a larger fraction of pores will be invaded by oil and will eventually become oil-wet high above the oil water contact than close to the oil water contact. In **Figure 6** we have plotted pore size distribution for typical lab values and for a height of 250 m above oil-water contact. From the figure, we observe that in the lab all the pores have been invaded by oil and a fraction of them has been converted to oil-wet pores, whereas in the reservoir, because of lower drainage pressure than in the lab, only the largest pores have been invaded and all of them have been converted to oil-wet pores.

In **Figure 2** we have plotted imbibition curve for Core 3 at different ageing time and drainage pressure, but kept the Amott-Harvey index constant. We clearly see no dramatic

change in the imbibition curve by going from two weeks to four weeks, even making the ageing time infinite does not change the imbibition curve dramatically.

DISCUSSION

We have used a bundle of tubes model to describe the porous rock. This is of course a crude simplification with regards to flow properties in a porous rock. A bundle of tubes model is simply parallel cylindrical tubes with no interconnection and the flow properties are sensitive to the location of oil-wet and water-wet regions. However, when it comes to drainage and ageing, we are only considering static equilibrium configurations. The fluids are not flowing. Based on the assumption that the fluids at any time are in equilibrium, there is hope that the bundle of tubes model will describe well normalized drainage and to some extent imbibition.

We have compared our model with a two-phase network simulator by Blunt et al. This simulator is freely available on the internet^[21]. The comparison has been done in the following way: the network simulator was run with the data provided with the simulator. In this case it was Berea sandstone. The output, among other things, was a drainage curve and imbibition curve. One part of the input to the network simulator is a set of pore- and throat radii, this set of radii can be used to make a pore size distribution. We could have chosen to fit a pore size distribution to the drainage curve as we did with the experimental results. We have instead used the pore and throat radii as input to the bundle of tubes model. In **Figure 1**, we have compared the result for bundle of tubes model and network model. T_{max} has been chosen to match the crossing point of the imbibition curve from the network model. The drainage pressure is determined by the network simulation as the maximal capillary pressure given into the network simulator. Clearly, there is a good match between the network and the bundle of tubes model. The drainage curve is slightly lower for the bundle of tubes model; this is obviously a consequence of no interconnection between the tubes. At any given capillary pressure all the tubes are available for oil invasion. A circular bundle of tubes model only allows piston type displacement. During water injection the filling process of a pore is dependent on the connecting pores[2, 3]. The entry capillary pressure for a water wet pore is expected to be lower (higher water phase pressure), compared with drainage. Clearly, the effect of connectivity would be to lower the imbibition curve, with respect to the water wet pore space. What we observe from Figure 1 and Figure 5 is that the predicted imbibition curve for the bundle of tubes model is higher in the water wet region than the network and experimental curves. Using this ageing model in a model of the porous medium with interconnecting pores would thus lower the imbibition curve.

The characteristic pressure is determined from the disjoining pressure curve as the first metastable maximum. The exact form of the disjoining pressure is not very well known

for crude oil and there seems to be some discrepancy between the DLVO formulation and experiment[23, 1, 4]. In this work we have simply put the characteristic pressure equal to zero. A motivation for doing this is that the drainage pressure used in real lab experiment is significantly higher than this maximum. However, the situation in the reservoir is different where drainage pressure (height above oil-water contact) is significantly lower. So there is reason to believe that the effect of disjoining pressure should be more important in describing wettability alteration at reservoir conditions.

CONCLUSIONS

We have developed a model for ageing and tested the model in a simple bundle of circular tubes model. The model has been compared with experimental results and a network model. The model reproduces qualitatively imbibition curves and Amott-Harvey indices comparable with experimental results. Apart from the pore size distribution, the model contains three parameters, drainage pressure, ageing time and a characteristic pressure. Ageing time has been determined from the crossing point of the drainage curve at the S_w -axis. The ageing time could also have been determined by resistivity experiment, as more and more water film collapse the resistivity will increase as a function of time^[9]. This line has not been investigated in this work, but could be the most promising way to find a good estimate of the ageing time.

Ageing time enters as a parameter in this model of wettability change. Therefore this model discriminates between lab and reservoir conditions by honouring ageing time. Ageing time in lab is finite whereas in the reservoir it is infinite. The model can then be used to interpret lab results and by correcting for ageing time one can obtain results valid at reservoir conditions. However in order to predict flow properties of porous media it is necessary to use the ageing model developed in this paper in a model of the porous media which contains interconnection of pores. This will be the subject of further work.

REFERENCES

- [1] S. Basu and M. Sharma, *Measurement of Critical Disjoining Pressure for Dewetting of Solid Surfaces*, Journal of Colloid and Interface Science, 181 (1996), pp. 443-455.
- [2] M. Blunt, *Physically-based network modelling of multiphase flow in intermediate-wet porous media*, J. Pet Sci. Eng, 1998, pp. 117-125.
- [3] M. Blunt, M. Jackson, M. Piri and P. Vavlatne, *Detailed physics, predictive capabilities and macroscopic consequences for pore-network models of multiphase flow*, Advances in Water Resources, 2002, pp. 1069-1089.
- [4] J. Buckley and Y. Liu, *Some Mechanism of crude oil/brine/solid interactions*, Journal of Petroleum Science and Engineering, 20 (1998), pp. 155-160.
- [5] J. Buckley and D. Lord, *Wettability and Morphology of Mica Surfaces after Exposure to Crude Oil*, Journal of Petroleum Science and Engineering, 39 (2003), pp. 261-273.

- [6] J. Buckley and J. Wang, *Crude Oil and Asphaltene Characterization for Prediction of Wetting Alteration*, Journal of Petroleum Science and Engineering, 33 (2002), pp. 195-202.
- [7] B. Derjaguin and L. Landau, Acta Physicochim. URSS, 14 (1941), pp. 633.
- [8] B. Derjaguin and E. Obuchov, Acta Physicochim. URSS, 5 (1936), pp. 1.
- [9] M. Fleury, *Advances in resistivity measurements using FRIM method at reservoir conditions. Applications to carbonates, SCA, Pau, France, 21-24 September 2003*, 2003.
- [10] G. Hirasaki, *Wettability: Fundamentals and Surface Forces*, SPE Formation Evaluation (1991), pp. 217-226.
- [11] R. Hughes and M. Blunt, *Network modeling of multiphase flow in fractures, Advances in Water Resources*, 2001, pp. 409-421.
- [12] J. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York City, 1985.
- [13] T. Kløv, P. Øren, J. Stensen, T. Lerdahl, L. Berge, S. Bakke, T. Boassen and G. Virnovsky, *Pore-to-Field Scale Modeling of WAG, SPE, Denver, Oct. 5-8, 2003*.
- [14] A. Kovscek, H. Wong and C. Radke, *A Pore-Level Scenario for the Development of Mixed Wettability in Oil Reservoirs*, SPE, Washington, Oct. 4-7 (1992), pp. 163-177.
- [15] A. Kovscek, H. Wong and C. Radke, *A pore-level scenario for the development of mixed wettability in oil reservoirs*, AIChE J., 39 (1993), pp. 1072-1085.
- [16] H. Man and X. Jing, *Pore Network Modelling of Electrical Resistivity and Capillary Pressure Characteristics, Transport in Porous Media*, 2000, pp. 263-286.
- [17] M. Morrow, H. Lim and J. Ward, *Effect of crude -oil induced wettability changes in oil recovery*, SPE Formation Evaluation, 1 (1986), pp. 89-103.
- [18] T. Patzek, *Verification of a complete pore network simulator of drainage and imbibition, SPE, Tulsa, April 3-5, 2000*.
- [19] C. Saliba, M. Robin, A. Cazabat and L. Cuiec, *Wettability changes by adsorption from crude oil and its heavier fractions, 2nd International Symposium on Colloid Chemistry in Oil Production (ISCOP'97)*, Rio de Janeiro, Mexico, 1997.
- [20] M. Tuller and D. Or, *Hydraulic conductivity of unsaturated fractured porous media: Flow in a cross-section, Advances in Water Resources*, 2003, pp. 883-898.
- [21] P. Valvatne,
<http://www.huxley.ic.ac.uk/research/PETENG/Perm/porereseach.htm>.
- [22] E. Verwey and J. Overbeek, *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam (1948).
- [23] X. Xie, M. Morrow and J. Buckley, *Contact Angle hysteresis and the Stability of Wetting Changes Induced by Adsorption from Crude Oil*, Journal of Petroleum Science and Engineering, 33 (2002), pp. 147-159.

ACKNOWLEDGEMENT

We acknowledge ConocoPhillips for financial support and permission to publish.

Table 1. Parameters entering in the calculation of drainage and imbibition curves of five different cores from the North Sea .

	Core 1	Core 2	Core 3	Core 4	Core 5
T_{Max}	0.22	0.22	0.22	0.005	0.005
$P_{c_{drain}}[kPa]$	183.4	184.9	182.7	4770.689	4465.734
P_c^{char}	0	0	0	0	0
α_1	$2.15 \cdot 10^{-5}$	$2.02 \cdot 10^{-6}$	$1.14 \cdot 10^{-6}$	$3.39 \cdot 10^{-8}$	$1.55 \cdot 10^{-8}$
γ_1	1.50	28.6	0.78	0.98	0.82
α_2	$1.35 \cdot 10^{-8}$	$8.10 \cdot 10^{-6}$	$8.85 \cdot 10^{-7}$	$1.48 \cdot 10^{-7}$	$1.36 \cdot 10^{-7}$
γ_2	0.32	37.2	35	11.3	13.6
ω	$1.72 \cdot 10^{-3}$	0.44	0.77	0.75	0.90

Table 2: Amott-Harvey index for Core 1-3

T_{Max}	I_A - Core 1	I_A - Core 2	I_A - Core 3
0.22	-0.09	-0.08	-0.02
0.19	0.008	0.02	0.08
0.16	0.114	0.134	0.195
Exp. value	0.007	0.014	0.287

Table 3: Different ageing time and drainage pressure for Core 3

$P_{c_{drain}}[kPa]$	T_{Max}	I_A
182.7	0.22 (~ 4-weeks)	-0.02
230	0.17 (~ 3-weeks)	-0.02
380	0.10 (~ 2-weeks)	-0.02

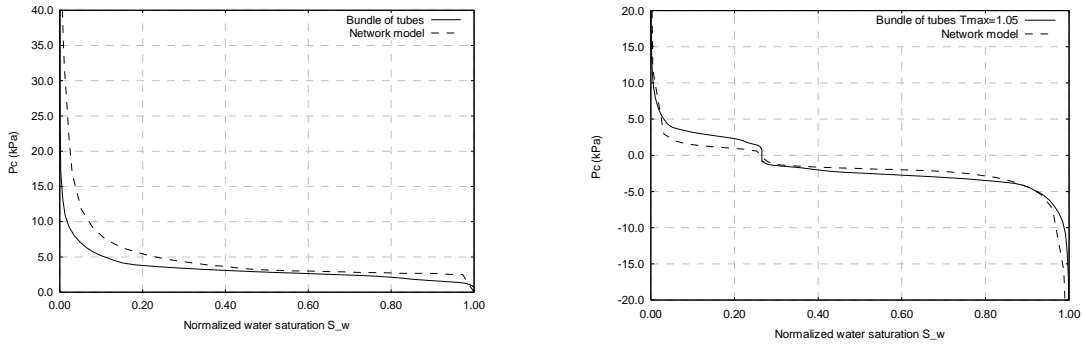


Figure 1: Normalized drainage (left) and imbibition (right) curve for network model and bundle of tubes model

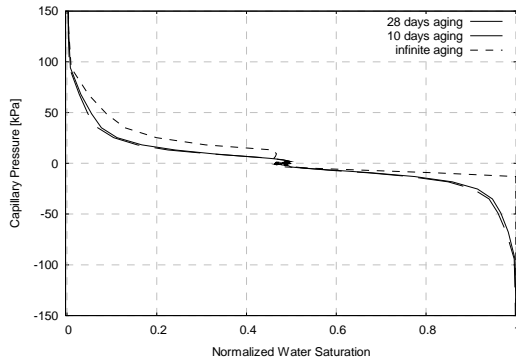


Figure 2: Imbibition curve for Core 3 at different ageing time and drainage pressure, but equal Amott-Harvey index.

Table 4: Physical properties of Core 1-5

	Abs. Perm. [mD]	Por.	Type
CORE 1	4094	0.250	Sandstone
CORE 2	8383	0.216	Sandstone
CORE 3	44.6	0.225	Sandstone
CORE 4	0.30		Carbonate
CORE 5	4.50		Carbonate

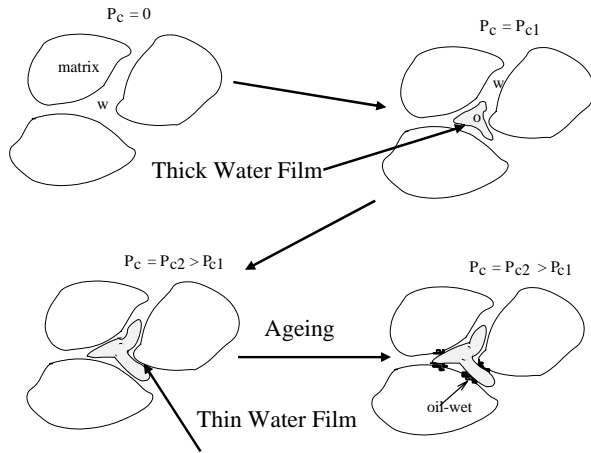


Figure 3: Primary Drainage and ageing in a pore, the black dots in the lower-right picture indicate oil-wet regions after ageing.

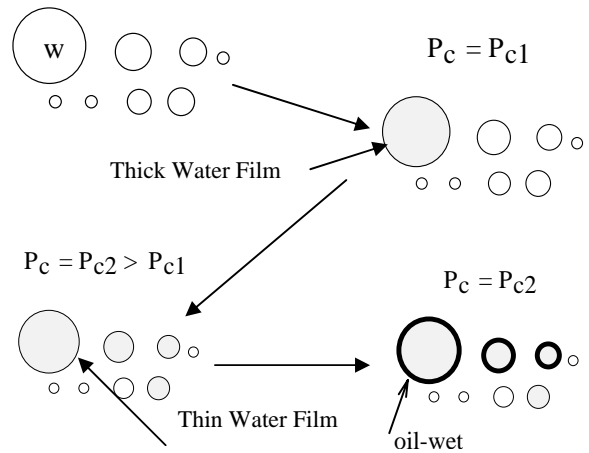
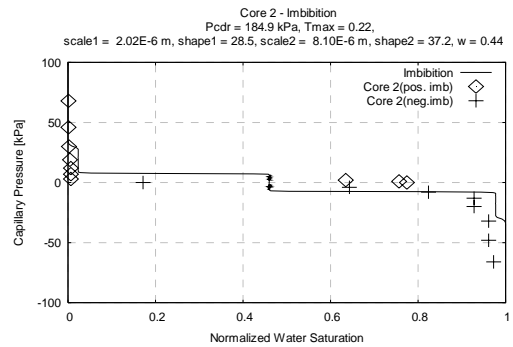
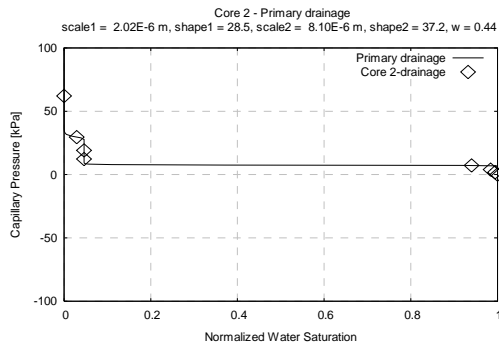
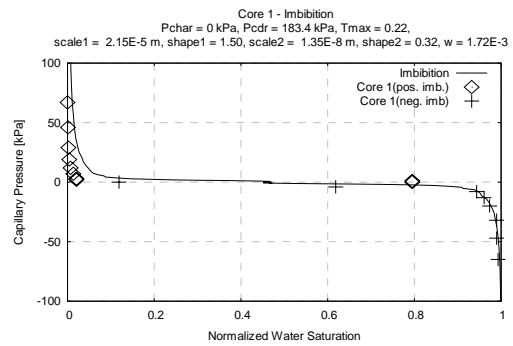
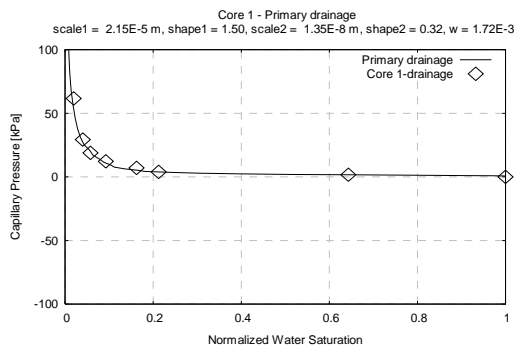


Figure 4: Drainage and ageing in a bundle of tubes model



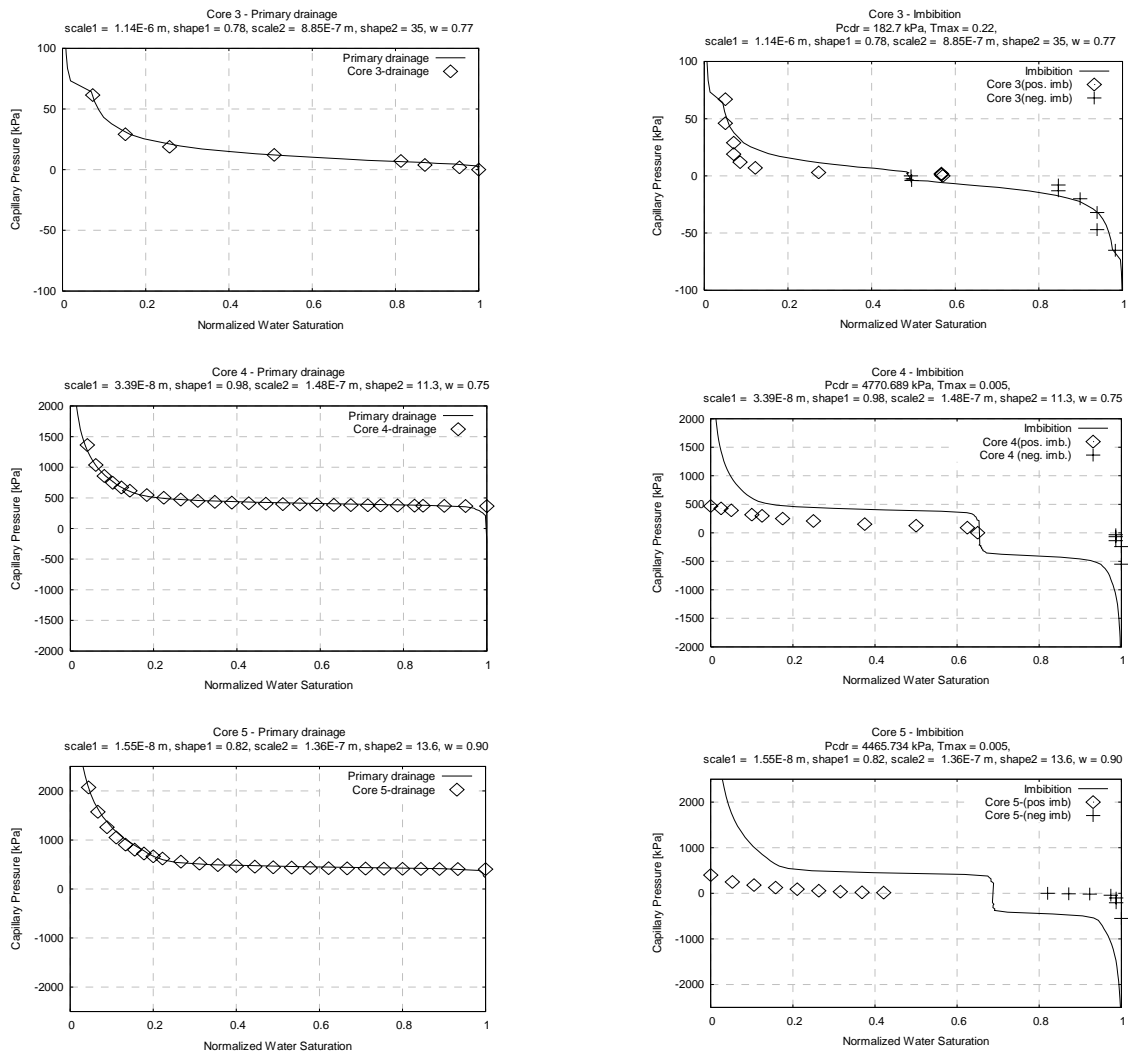


Figure 5: Experimental (points) and theoretical drainage curve (left) and imbibition curve (right).

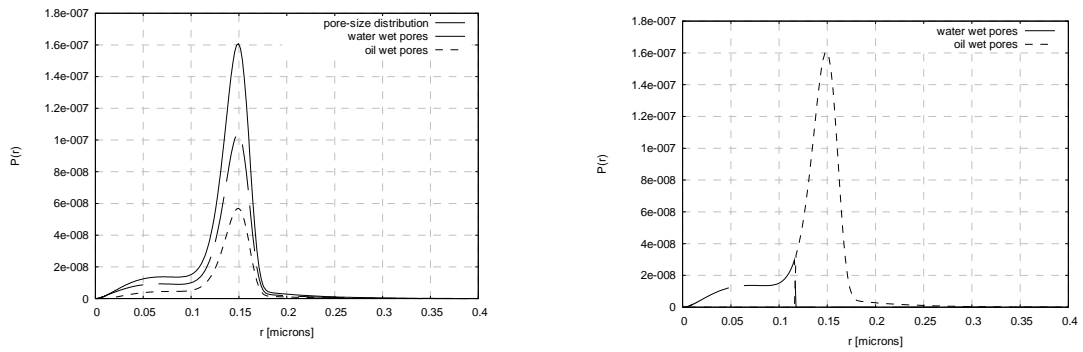


Figure 6: Pore size distribution after ageing: lab (left) and reservoir (right).