THE STRUCTURE OF RESIDUAL OIL AS A FUNCTION OF WETTABILITY ALTERATION USING PORE-SCALE NETWORK MODELLING

K.S. Sorbie, A.V. Ryazanov and M.I.J. van Dijke Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, UK

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ABSTRACT

In the water flooding of mixed-wet systems, oil may drain down to relatively low residual saturations and various studies have indicated that such low saturations can only be reached when oil layers in pore corners are included in the pore-scale modelling. Recently, the authors have developed thermodynamic criteria for oil layer existence in pores with non-uniform wettability which takes as input geometrically and topologically representative networks, to calculate realistic S_{or} values for mixed-wet and oil-wet sandstones. This work has recently been updated to include (i) the visualisation of the 3D structure of this residual oil, and (ii) a statistical analysis of this "residual/remaining" oil under a wide range of wettability conditions, which is reported for the first time in this paper.

This paper shows the qualitative trends in the structure of residual oil that are predicted as a function of wettability. Indeed, we are aware that mico CT studies are reaching the point where they can visualise the structure of (at least *part* of) the residual oil and we would like to publish these results before we "see the answer" for mixed-wet systems. The structure of residual oil for strongly water wet systems is well known (where residual = remaining oil) and our model agrees with this but this structure changes radically for mixed wet systems (where residual \neq remaining what do you mean with this inequality???) and this has not yet been visualised experimentally. The predictions in this paper can therefore be verified or refuted by appropriate experiments in the future.

We find that for more water-wet systems high final residual oil saturations are reached at relatively small amounts of water injected and this oil is present in the pores as bulk oil. On the other hand, for more oil-wet systems we find a slow decrease of the amount of remaining oil with increasing amounts of injected water. During the process, the remaining connectivity of the oil phase is increasingly provided by oil layers only, hence the slow drainage. The final residual oil saturation, only reached in the theoretical limit of an infinite amount of injected water, is almost entirely contained in large number of (relatively low volume) oil layers, which are present in pores of most radius sizes.

INTRODUCTION

The aim of all EOR methods is to mobilize oil trapped either locally by capillary forces and/or by large scale bypassing during waterflooding. It is the more local

"residual/remaining" oil that we focus on in this paper and the prediction of this residual oil saturation (S_{or}) after waterflooding is very important before carrying out any EOR process. The mechanism through which a particular EOR method, such as gas displacement, actually works to reduce residual oil depends in turn on precisely *how* that oil is trapped at the pore scale. In this respect, pore-scale network modelling can be used to estimate both the nature of the trapped residual oil and the relevant flow parameters in

Pore scale network modelling is a well established approach for calculating the small scale petrophysical functions of two- and three-phase flow through porous media, such as capillary pressure and relative permeabilities [1,2,3,13,16,21]. Recently, it has been possible to construct direct models of the actual pore space, either numerically or by micro-CT scanning, from which more idealised geometric pore networks can be extracted, as shown in Figure 1 [8,9,14,15,22]. These network models can then be used in physics-based calculations which model the pore scale displacement events (piston-like displacements, snap-off, layer formation/collapse etc.).

its subsequent mobilization, if the correct physics of oil drainage are properly included.

In modelling the two phase flooding cycle from primary drainage (PD) to S_{wi} followed by "ageing" (to alter wettability to some specified state) and the subsequent imbibition (IM), we reach a value of "residual oil", S_{or} .



Figure 1: (a) 3D CT image of a Berea sandstone sample; (b) the Network extracted from the 3D CT image of the Berea sandstone sample (*BereaCT*) [8].

Precisely where do we stop the imbibition process in network modelling is an open issue. For example, we may simply stop the process when a target S_{or} is reached and this is clearly not a prediction. Alternatively, we may continue the network simulation of imbibition to a specified target capillary pressure, P_c , or finally, we may proceed until no further pore-scale displacements are possible. If we wish to predict the residual oil value for a given case, then it is essential that we have a good description of the pore-scale physics of the imbibition process for systems of arbitrary wetting state. This must include a mathematical description of piston like water \rightarrow oil (w \rightarrow o) displacements, snap-off , pore-body filling (again w \rightarrow o) events and oil layer formation/collapse events [12]. Various possible configurations that can exist during imbibition in the cross-section of a model triangular pore (bond) are as shown in Figure 2 [10]. Figure 2(a) shows the



fluid configuration with bulk oil (in the pore centre) and water in the corners, whereas Figure 2(b) shows the configuration with bulk and corner water, separated by oil layers.

Figure 2: Three fluid configurations denoted (a) – (c) which could exist in an angular pore during imbibition. *Red*—means oil phase, *blue*—water phase, *brown lines*—surfaces of altered wettability on which a contact angle, θ_{ow} , may be specified.

Van Dijke and Sorbie [20] obtained accurate thermodynamically derived criteria for oil layers existence in pores with non-uniform wettability caused by ageing, which is more restrictive than the previously used geometrical layer existence criteria [6,19]. Regions of existence of oil layers are mapped in Figure 3, which shows where oil layers can and cannot exist as functions of the local P_c and wettability (contact angle, θ_{ow}). The oil layers exist in the shaded areas in Figure 3 and the main point to note is that the geometrical layer existence criteria allow a much larger region of oil layer existence than the thermodynamic criteria. This over prediction of layers in the geometric case very often leads to a prediction of zero Sor since oil can always escape in the network model through the many stable oil layers indicated by this model. Alternatively, the thermodynamic oil layer criteria lead to much smaller regions of oil layer stability and hence more often predicts a non-zero Sor as the flood (i.e. the pore scale network calculation) proceeds to completion. Recently, Ryazanov et al [17] have included these thermodynamic criteria in a two-phase pore network model, which takes as input geometrically and topologically representative networks, to calculate realistic Sor values for mixed-wet and oil-wet sandstones.



Figure 3: Dimensionless capillary entry pressures Pc versus advancing contact angle θa for the various displacements, including oil layer formation/collapse models using (a) thermodynamic criteria [20] and (b) geometrical criteria [6,19]. *Vertical dashed gray* lines indicate water invasion scenarios, i.e. decreasing Pc, for different advancing contact angles. In scenario 1 for a weakly oil-wet pore no layers form, whereas in scenario 2 for a strongly oil-wet pore oil layers exist in a limited regime of Pc values (*shaded* region).

The actual predictions of residual oil for the thermodynamic and geometric layer criteria for the Berea network in Figure 1 are shown in Figure 4(a), where 2 variants of the geometric criteria are used (see [17] for details).



Figure 4: Figures showing (a) S_{or} vs. advancing contact angle, θa , for the three oil layer existence scenarios including the thermodynamic criteria, and 2 variants of the geometrical criteria, and (b) S_{or} vs. advancing contact angle, θa , for the thermodynamic criteria at various specified end point capillary pressure values, P_c [17].

- 1. Clearly, the more restrictive thermodynamic oil layer formation/collapse criteria lead to larger values of S_{or}, i.e. they represent a "final" residual oil which is technically the end of the pore-scale flooding cycle by capillary displacement. Further oil mobilisation (and hence Sor reduction) could only take place by greatly increasing the viscous forces, this is not generally included in network models used for mixed and fractionally wet systems. However, if we furthermore specify the end point capillary pressure of the water \rightarrow oil imbibition process, then we may arrive at different levels of S_{or} as shown in Figure 4(b). This final residual oil shows quite complicated but understandable behaviour as a function of average contact angle in the network. However, the central concern of this paper is to ask what the predicted *structure* of this residual oil is; i.e. (i) where is the oil trapped in terms of the pore sizes (big pores or small pores?), Why you do not look at experimental evidence, at least for water-wet systems, to gauge your simulation results? (eg. look at the results in the papers : I. Chatzis, N.R. Morrow, and H.T. Lim (1983): "Magnitude and Detailed Structure of Residual Oil", SPE Journal, 33, 2, pp. 311-326. doi: 10.2118/10681-PA:
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(ii) in what form is it held – in the pore centres (as in Figure 2(a)) or in layers (as in Figure 2(b)), and (iii) is the oil a "final" residual in the sense noted above, i.e. is it at an end point where no more pore-level capillary imbibition events can occur or if the P_c is increased can more oil be produced thus reducing S_{or} further

THE STRUCTURE OF THE RESIDUAL OIL

We now consider the structure of the residual oil as a function of wettability for the Berea network. In fact, we derive an Amott-Harvey index (I_{ow}) from the network model calculations for comparison with residual oil experiments and this is done below ($I_{ow} = 1$ is strongly water wet and $I_{ow} = -1$ is strongly oil wet); see [4]. Using the pore scale network model calculated relative permeabilities, we can predict the oil which remains during a 1D water flood using Buckley-Leverett theory, as described by McDougall and Sorbie [13]. This allows us to calculate a remaining oil "S_{or}" as a function of pore volume (PV) of water injection in the waterflood where the genuine, final S_{or} (in the sense described above) would be reached after an infinite number of PV had been injected into the system.

The results of this type of calculation are shown in Figure 5 where the calculations of Recovery Factor (RF) and " S_{or} " are shown as functions of wettability (I_{ow}) in 3 columns where (a) is at 20PV throughput, (b) is at 3PV and (c) breakthrough (BT); the corresponding experimental data is also shown in these figures at each PV [7]. Note that all studied cases are fractionally wet in the sense that they all have non-zero fractions of oil-wet and water-wet pores. Obviously, the oil-wet cases have a much larger fraction of oil-wet pores. Details of the wettability distributions can be found in [18]. The distributions have been obtained through matching to the experimental data at breakthrough. Then the calculations for 3 and 20 PV throughput are actual predictions without further alterations of the parameters, and these show excellent agreement with the experimental data.

Four wettability conditions (I_{ow} values) are highlighted for detailed study in Figure 5(a) and are denoted **N01** ($I_{ow} = -0.47$, moderately oil wet), **N09** ($I_{ow} = 0.13$, near neutral wet), **N11** ($I_{ow} = +0.31$, weakly water wet) and **N14** ($I_{ow} = +0.59$, moderately water wet). Table 1 shows these 4 cases in terms of their I_{ow} values and calculated S_{or} values at various PV throughputs from BT, 3PV, 20PV and infinite PV.



(a) 20 PV throughput (b) 3PV throughput (c) at breakthrough Figure 5: Calculated Recovery Factor (RF) and " S_{or} " vs. I_{ow} using the pore-network model of the Berea sample (in Figure 1) at (a) 20PV throughput, (b) 3PV throughput and (c) at breakthrough (BT). The infinite PV case –red line with dots - is shown in each figure and also the relevant experimental data are shown at each PV throughput. Experimental data are from [7] - circles.

We now consider the structure of the oil in the pore network for the S_{or} values at 20PV of water injection and at infinite PV injection only for the 4 cases N01, N09, N11 and N14 (see Table 1). This is shown in Figures 6, 7 and 8 for these 4 cases at 20PV throughput; see notation in the caption and discussion below.

Table 1: Details of the 4 cases N01, N09, N11 and N14; I_{ow} values and remaining oil " S_{or} " values at various PV throughputs.

low	-0.47	0.13	0.31	0.59
Sor	N01	N09	N11	N14
BT	51.9%	28.8%	28.6%	28.5%
3PV	40.0%	22.5%	22.0%	24.7%
20PV	28.2%	15.9%	15.6%	24.7%
InfPV	2.0%	4.1%	8.4%	24.7%



The visibility of structure is very foggy in these figures

Figure 6: The structure of the remaining oil " S_{or} " at 20 PV throughput for cases **N01** ($I_{ow} = -0.47$), **N09** ($I_{ow} = 0.13$), **N11** ($I_{ow} = +0.31$) and **N14** ($I_{ow} = +0.59$), where we denote BO (red) + BW (blue) = Bulk Oil + Bulk Water; BO (red) + OL (yellow) = Bulk Oil + Oil Layers, BO (red) = Bulk Oil only and OL (yellow) = Oil Layers only. The lower figure is a high resolution image of **N01** BO-OL.

Figure 6 shows *all* the pores that contain bulk oil (BO – red) and oil layers (OL – yellow) present in each example (N01, N09, N11 and N14) at 20PV of water injection in the waterflood. Note that pores containing bulk water (BW - blue) may contain oil layers as well. In Figure 6, recall that the samples in order left to right (i.e. N01 \rightarrow N09 \rightarrow N11 \rightarrow N14) go from being more oil wet to more water wet. Figures 7 and 8 show respectively only the pores that contain *non-trapped* and *trapped* oil (BO – red) and oil layers (OL – yellow) present in each example (N01, N09, N11 and N14) at 20PV of water injection in the waterflood.

Figure 7: The structure of the **non-trapped** remaining oil " S_{or} " at 20 PV throughput for cases **N01** ($I_{ow} = -0.47$), **N09** ($I_{ow} = 0.13$), **N11** ($I_{ow} = +0.31$) and **N14** ($I_{ow} = +0.59$) - notation as in Figure 6.

Figure 8: The structure of the **trapped** remaining oil " S_{or} " at 20 PV throughput for cases **N01** ($I_{ow} = -0.47$), **N09** ($I_{ow} = 0.13$), **N11** ($I_{ow} = +0.31$) and **N14** ($I_{ow} = +0.59$) - notation as in Figure 6.

Figure 9: The structure of the **residual** oil S_{or} at inf PV throughput for cases **N01** ($I_{ow} = -0.47$), **N09** ($I_{ow} = 0.13$), **N11** ($I_{ow} = +0.31$) and **N14** ($I_{ow} = +0.59$) - notation as Figure 6.

By *trapped* oil (Figure 8) we mean the oil (and oil layers) visualised in this figure is the isolated oil (and layers) that will still be present at infinite PV of injected water throughput i.e. at the end of the flood where no more capillary displacements are possible. Correspondingly, the *non-trapped* oil (Figure 7) is that oil (and oil layers) at 20PV of throughput, which may still be produced between 20PV and infinite PV of injection water throughput in the pore network model imbibition simulation. Figure 9 shows the true residual oil at infinite PV of injected water, i.e. all this oil (in both bulk pores and oil layers) is trapped.

The sequence of visualisations from Figure 6 to Figure 8 tells a fairly clear story about the nature of "residual oil" as we go across the 4 examples from a more oil wet to a more water wet system. The remaining oil at 20 PV throughput is clearly different in nature as a function of wettability (I_{ow}) in that, *as we go from oil wet to water wet* (i.e. N01 \rightarrow N09 \rightarrow N11 \rightarrow N14):

- (i) The remaining oil changes in nature from being some bulk oil but many layers (N01) to being almost entirely bulk oil and very few layers (N14) (Figure 6);
- (ii) The trapped oil is very low or zero in strongly oil wet systems and this is clearly due to the persistence of oil layers which allow oil drainage down to very low levels (Figures 7 and 8); only at infinite PV a slightly larger trapped saturation arises, but this is almost entirely contained in oil layers (Figure 9);
- (iii) In more water wet case (N14), the amount of trapped oil is much larger and it is mainly present as bulk oil with few oil layers. Indeed, it is the absence of

these oil layers that allows the oil blobs of bulk oil to become cut off (trapped) and therefore not amenable to capillary displacement processes.

(iv) As expected, the intermediate cases (N09 and N11) show behaviour in between the end member cases, with remaining oil at 20PV being a combination of some bulk oil and layers, but these cases do show more significant non-zero final residual oil at infinite PV throughput.

Figure 10: The structure (top line) – colours as in Figure 6 -, the number (occupancy - middle line) statistics and the volumetric (lower line) statistics of the **residual** oil S_{or} at infinite PV throughput, as a function of pore (node and bond) radius, for cases **N01** ($I_{ow} = -0.47$), **N09** ($I_{ow} = 0.13$), **N11** ($I_{ow} = +0.31$) and **N14** ($I_{ow} = +0.59$) In the occupancy statistics red indicates the number of pores entirely occupied by bulk oil (BO), orange indicates the number of pores occupied by bulk water, oil layers and corner water (BOCW), yellow indicates the number of pores that are entirely occupied by bulk water (BWLOCW) and blue indicates the number of pores that are entirely occupied by bulk water (BW). In the volumetric statistics a similar colour scheme is used for the volumes of the individual occupancies, with yellow indicating oil layers (LO) and light blue indicating corner water (CW).

From the visualisation it is difficult to estimate the actual volumes of oil involved in bulk and in layers. Note that oil layers only occupy a small fraction of the volume of given pore. The number and volumetric statistics of the residual oil calculation at infinite PV are shown in Figure 10 for the 4 wettability cases described above. It can be seen from the occupancy statistics in Figure 10 that for the more oil-wet cases oil layers are present in all pore sizes, but that bulk oil is only present in the smallest pores. In volumetric terms the residual oil is in the smallest pores in the most oil wet case (N01), this is spread across pore sizes in the intermediate cases (N09 and N11) and it tends to be in the larger pores for the most water wet case (N14).

DISCUSSION AND CONCLUSIONS

In this paper, we have applied pore-scale network modelling of waterfloods to make some semi-quantitative predictions of the *structure* of residual oil in pore systems of mixed wettability. The predicted structure of "S_{or}" as a function of wettability (I_{ow}) shows that there are clear differences as the system goes from moderately oil wet to moderately water wet. The remaining oil changes in nature from being some bulk oil but many oil layers (oil wet, N01) to being almost entirely bulk oil and very few layers (moderately water wet, N14) with a transition between these two end points being seen for intermediate cases (N09, N11).

In practical terms, we must consider what the relevance of these results is to an experimental core water flood. Although, we are able theoretically to calculate a final residual when all pore scale capillary displacements have actually stopped (i.e. at infinite PV throughput), this situation is probably *not* reached in an actual core flood. In practice, there is some practical but not well defined "cut off" capillary pressure where we have effectively reached what is referred to in an experiment as "residual oil". This is what is calculated in Figure 4(b) which shows " S_{or} " as a function of final $P_{c.ow}$. What is actually happening in an experimental core flood is that the fractional flow of oil is simply so low that the time (or PV throughput) required to get to the lowest possible oil saturation is impractically long. The corresponding relative permeability, k_{ro} , is very low, say 10^{-6} – 10^{-10} , as the remaining oil is mainly connected through oil layers, which have very low conductances as compared to the conductance of bulk oil. Hence, the predictions on the distribution of residual oil should probably be taken at some defined PV throughput or at some chosen final P_{c,ow}. However, theses final chosen values will be rather arbitrary which implies that the exact numerical prediction of the specific value of "S_{or}" for a given mixed wet rock is not possible i.e. it is an arbitrary choice which gives a certain "S_{or}" but another choice would give a different value. This arbitrariness of the numerical value of "Sor", however, does not stop us from making testable semi-quantitative predictions on the *structure* of the residual oil as we do in this paper. The predictions on the structure of the "S_{or}" described above are all perfectly testable experimentally if the distribution of the remaining oil can be imaged and preliminary results of this type have already been presented for water wet rocks [11]. However, it will not be straightforward to image oil layers and some other more indirect methods such as NMR (T1/T2 distributions) may have to be employed to infer the presence of oil layers [5].

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