

# MEASUREMENTS OF REMAINING OIL SATURATION IN MIXED-WET CARBONATES

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## ABSTRACT

We age a selection of carbonate cores, including calcite quarry limestones and field samples using organic acid in order to alter the wettability state in a controlled way and reproducible manner to a mixed-wet state. Different initial oil saturations are established using a porous plate technique. We then measure the degree of spontaneous imbibition and the remaining oil saturation as a function of pore volumes of water injected.

We observe that the amount of spontaneous imbibition decreases with an increase in initial oil saturation, while the remaining oil saturation can decline to very low values when 20 or more pore volumes of water are injected. This behaviour is representative of mixed-wet systems and has been observed previously (Salathiel, 1973).

We find a non-monotonic trend between initial oil saturation and the remaining oil saturation after 20 PV injected (which we call the residual saturation).

## INTRODUCTION

Understanding trapping mechanism is important for applications in enhanced oil recovery (EOR) and carbon capture and storage (CCS). In EOR we design the process to leave as little residual oil behind as possible, while for CCS we do the opposite: we wish to maximize the amount of CO<sub>2</sub> trapped by the host brine. This paper will study mixed-wet media, which are thought to comprise at least 60% of the world's oil reservoirs (Anderson, 1986).

Pore structure and wettability are two of the main factors affecting capillary trapping. Experimental and pore-scale modelling studies have found a monotonic increase of residual non-wetting phase saturation,  $S_{nwr}$ , with the initial non-wetting phase saturation,  $S_{nwi}$  in a water-wet medium (El-Maghraby and Blunt, 2013; Land, 1968; Spiteri *et al.*, 2008). However, mixed-wet systems have received relatively little attention. Salathiel (1973) demonstrated that in a mixed-wet sandstone, the remaining oil saturation was a function of the pore volumes of water injected. It was shown that even after injecting 5,000 pore volumes, the oil saturation continues to decrease below 10%. The underlying reason is that oil flow through connected films which is a slow process but leads to very

low oil saturations. This contrast with water-wet media, where the oil as non-wetting phase disconnects and gets immobilized and the residual saturation can be achieved instantly at or near water breakthrough (Anderson, 1987). Hence, the only way to get to the residual saturation is by increasing the rate to overcome the capillary end effect (Masalmeh, 2012).

In this paper we present an experimental study of capillary trapping under both water-wet and mixed-wet conditions for three different carbonate rocks, extending the work of Tanino and Blunt (2013) on Indiana limestone.

## EXPERIMENTAL METHODS

**Cores.** We use three different types of carbonate rock in our study. **Estailades**, from France, is an upper cretaceous bioclastic limestone, which contains 99% calcite ( $\text{CaCO}_3$ ) and traces of dolomite and silica. The porosity,  $\phi$ , measured on different cores from the same block ranges from 27-28% and permeability,  $k$ , from 170-330 mD. **Ketton** is an oolitic limestone from the UK comprised of 99.1% calcite and 0.9% quartz. The porosity ranges from 22-23% with a high permeability from 2.1-3.6 D. **Portland** is another standard English quarry rock. It is an ooparite limestone of 96.6% calcite and 3.4% quartz. The porosity is around 18% and the permeability from 4-12 mD. All the cores used were 3.8 cm in diameter and 7.5 cm in length.

**Core and Brine Preparation.** We measure the porosity using Helium pycnometry, the permeability using  $\text{N}_2$  (correcting for the Klinkenberg effect).

For the brine preparation, we use 5 wt. % of NaCl and 1 wt. % KCl with a molality of  $1.05 \text{ b} / \text{mol.kg}^{-1}$ . In addition, we add smaller samples of the carbonate rock to the mixing of the brine in order to establish chemical equilibrium between the brine and rock and eliminate any further reaction with the rock.

The core is inserted into a Hassler cell with a cylindrical confining pressure and we vacuum for overnight. In parallel, we insert the brine into a vacuum chamber and we vacuum overnight. We also vacuum saturate the porous plate.

### Water-wet scenario

**Brine Saturation.** We set the confining pressure with  $\text{N}_2$  to be 1.5 times higher than the pore pressure. We inject 5 PV of degassed brine at an average flow rate of 2.5 ml/min until we see no changes in the differential pressure. We then decrease the pore and confining pressures slowly to zero. We then insert the brine-saturated porous plate downstream with a filter paper between the core and the plate. Finally, we inject another 5 PV of degassed brine.

**Primary Drainage.** We inject n-decane (non-wetting phase) at a constant capillary pressure. The selection of the capillary pressure depends on the mercury capillary pressure data. In brief, we select a capillary pressure in the transition zone and we select

different pressures to establish different initial oil saturations. The porous plate retains the n-decane and only allows the brine to pass.

**Spontaneous Water Imbibition.** We reduce the pore and confining pressures to zero. We remove the core and weigh it and then insert it into a custom-made Amott cell. We monitor the spontaneous water imbibition until no further n-decane is produced at the top of the cell. Then we take the core out, weigh it and re-insert the core in the core holder for waterflooding.

**Waterflooding (Forced Water Injection).** After extracting the core from the Amott cell, we insert the core again into the Hassler cell and apply confining pressure. We inject 5-10 PV of degassed brine until we reach the remaining oil saturation. The injected flow rate is 0.1 ml/min giving a capillary number of  $6.0 \times 10^{-8}$ . We monitor the amount of n-decane produced.

### **Mixed-Wet Scenario**

To alter the wettability of the rock to a mixed-wet state at ambient conditions, we add 1.5 wt. % of cyclohexanepentanoic acid in n-decane. This approach has proven (Wu et al., 2008) to be a quick and efficient way to alter the wettability to a more oil-wet state. The procedure of the mixed-wet coreflooding experiments is exactly the same as the water-wet experiments discussed above; however, the only differences are that instead of injecting pure n-decane, we inject n-decane with 1.5 wt. % of cyclohexanepentanoic acid, place the altered core in the Amott cell for a duration of 30 days or more, and we then waterflood the core with up to 20 PV of brine. The waterflood starts at 0.1 ml/min for 5 PV and then we increase the flow rate gradually to reach up to 30 ml/min for Estailades and Ketton. However, for Portland we inject up to 0.35 ml/min since it has a very low permeability and increasing the flow rate will build up the pressure too high to be able to confine it.

## **RESULTS AND DISCUSSION**

The main results of this study are shown in Figure 1. For the water-wet systems we see a significant recovery from spontaneous imbibition, as expected. For the cores with altered wettability, spontaneous imbibition produces less than 5% of the initial oil in place, with further recovery as more and more brine is injected except for Ketton. This is due to the slow drainage of connected oil layers in the pore space (Salathiel, 1973).

In our work, we notice unexpected trend in remaining oil saturation with initial saturation: initially there was an increase, then a decrease (as the oil became better connected through layers) and then an increase again at the highest initial saturations for Estailades. This matches the conclusion reached by Tanino and Blunt (2013), using the same procedure for Indiana. For Portland, we see the same behaviour; however, we need inject at higher flow rates to reach to the residual oil saturation. For Ketton, we do not see

the effect of wettability alteration on Ketton which might be due to its high permeability as the entire volume of oil is recovered from spontaneous imbibition.

## CONCLUSIONS

We have presented a methodology for the study of waterflood recovery in carbonates, combining a reproducible and instant method for ambient-condition wettability alteration. We see significant recovery by spontaneous imbibition in water-wet rocks, with less imbibition, but continued recovery with brine injection in samples of altered wettability, as expected. We see significant recovery by spontaneous imbibition in water-wet rocks, with less imbibition, but continued recovery with brine injection in samples of altered wettability, as expected. We find a non-monotonic trend between initial oil saturation and the remaining oil saturation after 20 PV injected at high flow rates. In future work, we will extend our experimental study and, in combination with the numerical and analytical analysis, provide a predictive framework for understanding waterflood and imbibition recovery in carbonates of different wettability.

## ACKNOWLEDGEMENTS

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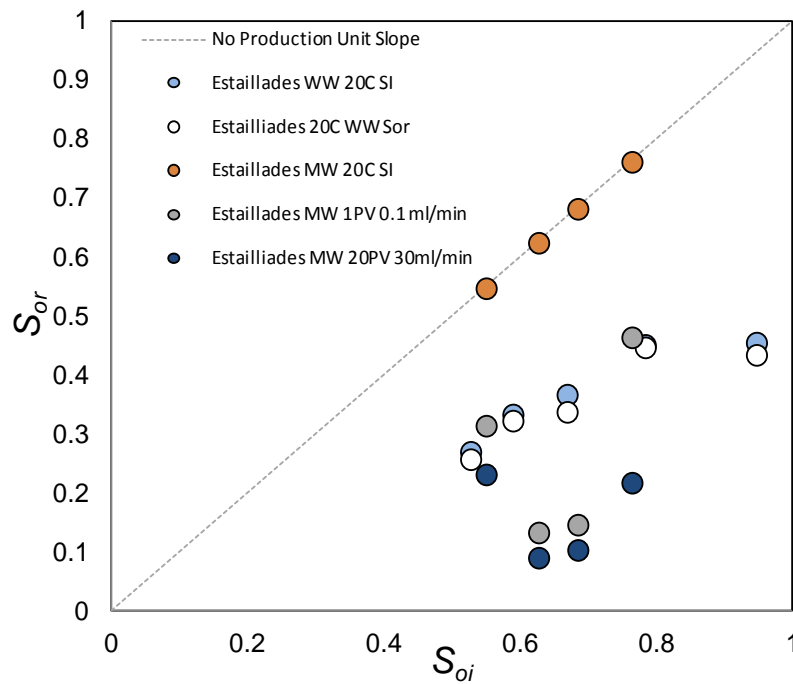
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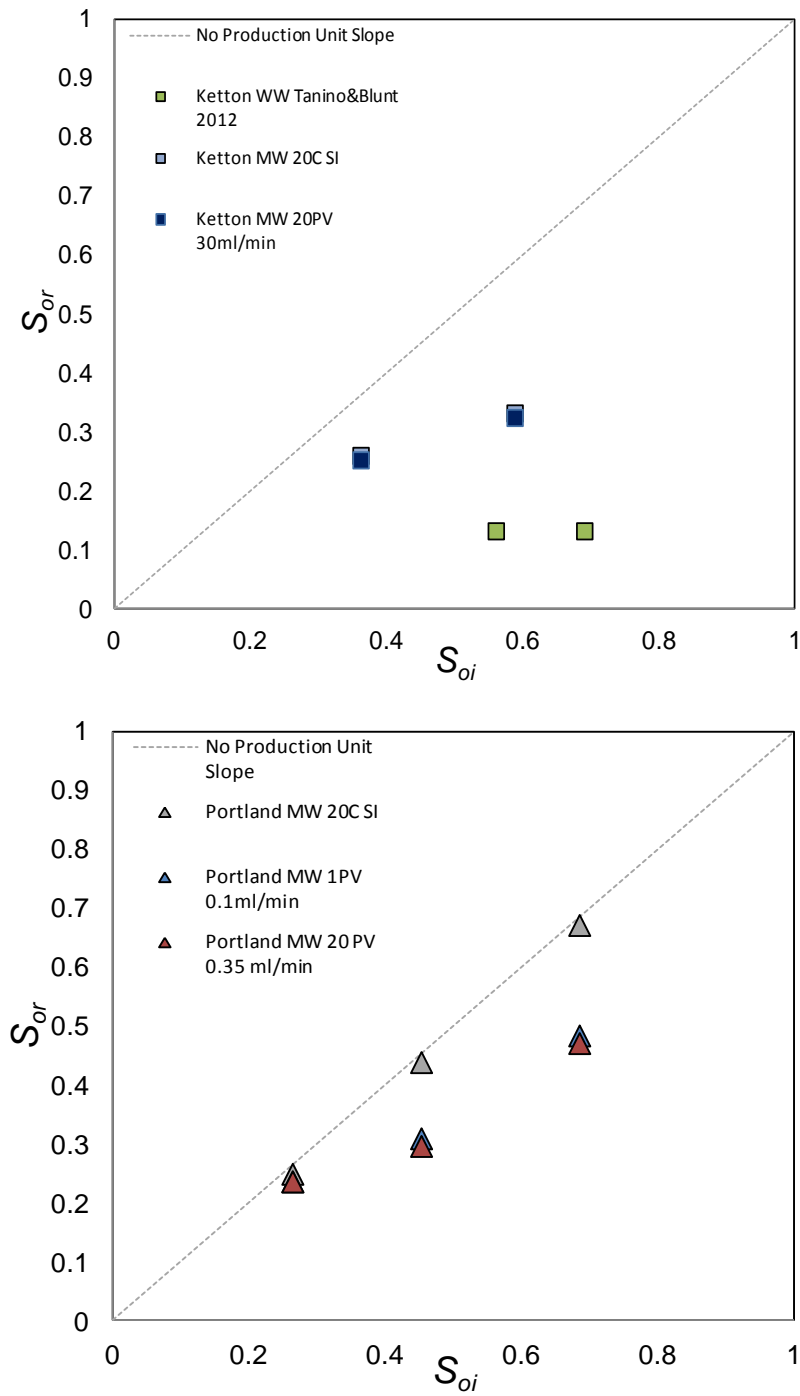


Figure 1. Remaining oil saturation as a function of initial oil saturation (“trapping curve”) for water-wet and mixed-wet Estallades (top), Ketton (middle), and Portland (bottom) core samples.