

## **CAPILLARY SEAL OR PERMEABILITY BARRIER: FIELD, EXPERIMENTAL AND THEORETICAL CONSIDERATIONS OF CAPROCK WETTING STATE.**

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Oilfield caprocks are generally assumed to be water wet with high capillary entry pressures preventing the leakage of oil from the underlying reservoir. Column heights are then estimated by measurement of a critical pore radius, use of assumed oil-water interfacial tensions and contact angles, and the assumption that the pore system is water-wet. However, under what circumstances is the assumption of water-wet caprocks actually valid?

Over the past few years we have been looking at the way in which petroleum non-hydrocarbons such as phenols (hydrophilic organic oxygen compounds) and carbazole derivatives (more hydrophobic nitrogen compounds) partition between oil, water and mineral surfaces in geological systems (Larter and Aplin, 1995; Larter et al, 1996; Taylor et al, 1997; Bennett and Larter, 1997). These studies indicate that many non-hydrocarbon compounds partition substantially from oil to either/or both water and mineral surfaces, with the implication that the wetting state of a rock may change after contact with oil. Recent data from experimental corefloods, coupled with (a) theoretical considerations of wetting state and (b) field studies of leaking caprocks, support this assertion. Here, we review this body of work and suggest that there is substantial doubt as to the assumption that mudstone caprocks remain water wet after contact with oil.

### ***Field Studies***

Studies of leaking caprocks on the Norwegian margin oilfields indicate that the petroleum retained within the caprocks is substantially enriched in carbazoles compared to the reservoir oil (Bond, 2001). These data indicate (a) the passage of multiple volumes of oil through a substantial fraction of the caprock volume, and (b) the sorptive removal of polar compounds by the caprocks.

### ***Experimental Studies***

Core floods through clay rich, microDarcy range permeability rocks such as siltstones (intermediate in pore properties between true seals and reservoir rocks), carried out under realistic subsurface conditions, show that many non-hydrocarbons are quickly removed from migrating oils. The results indicate that small hydrophilic molecules such as phenols are very rapidly removed and strongly retained by interaction with the cores (Figure 1, after Larter et al., 2000). Comparison of the molecular composition of the oil exiting the core with that injected into the core shows that it is predominantly low molecular weight polar compounds that are removed, and that many of these are multifunctional compounds with mixed nitrogen, oxygen (and sulphur) functionality (Figure 2). Estimates of the wetting state of the core were made by examining the nature of fine water droplets sprayed onto the core using an environmental scanning electron microscope. This showed that the initially water wet inlet the core had become oil wet during the experiment. The oil wetness of the core decreased towards the outlet of the core.

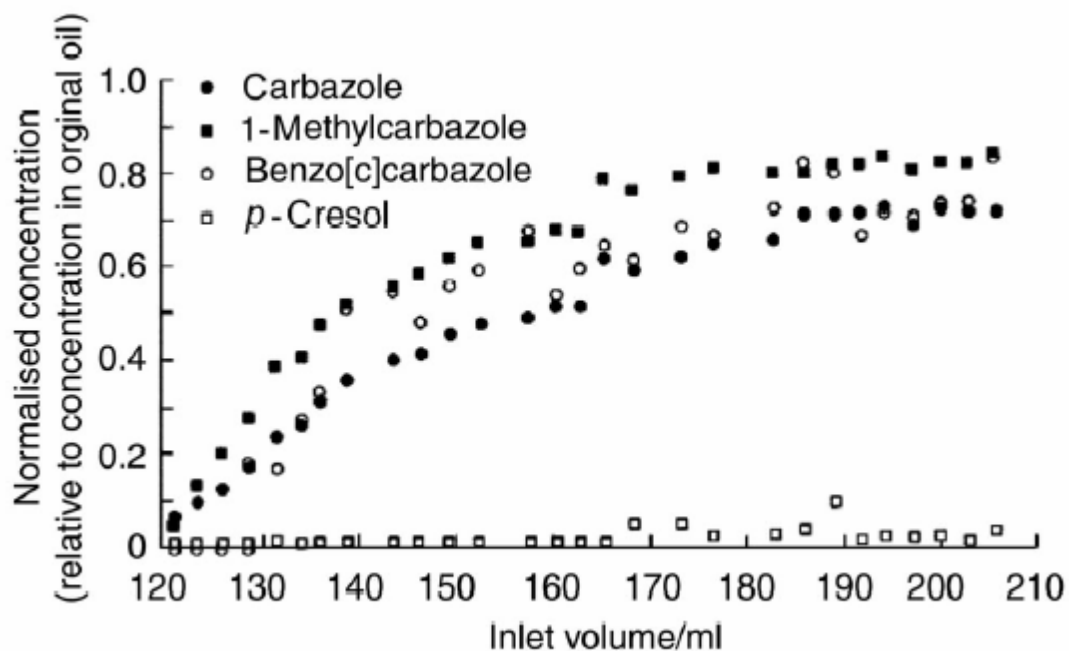


Fig. 1. Variation in concentrations of selected representative nonhydrocarbons in oil samples collected at a siltstone core outlet during a coreflood using 41° API gravity oil (modified after Larter et al, 2000). Concentration data has been normalised to values obtained for the original (input) oil. Note that phenols (as exemplified here by p-cresol) show much stronger depletion than carbazole compounds, being strongly retained in the core. The first oil eluted from the core after about 120ml of oil had been injected.

### ***Theoretical Considerations***

The extreme difficulty of directly measuring the wetting state of nm- $\mu$ m size caprock pores highlights the importance of predicting wettability from fundamental chemical considerations. Van Duin and Larter (2001) used molecular dynamics (MD) simulations to study the phase behaviour of organic-water mixtures in the presence of quartz and calcite surfaces. Changing the polarity of the organic phase from (a) a charge-neutral cyclohexane phase to (b) an apolar carbazole phase, (c) a polar phenol phase and (d) a highly polar acetic acid phase, results in distinct changes in the association of the organic phase with the mineral surface. Cyclohexane and carbazole form discrete organic phases, removed from mineral surfaces by a water film. Phenol and acetic acid are sufficiently soluble in water to penetrate water films and compete with the water molecules for mineral surface adsorption sites. This is consistent with the rapid removal of phenols and other small hydrophilic moieties during the coreflood. Further MD simulations with pre-adsorbed phenol compounds on a calcite surface suggest that these small polar molecules can have a profound impact on surface wettability, making the mineral surface accessible to even completely non-polar compounds including hydrocarbons. This provides strong support for a two-stage process by which the wettability of mineral surfaces change as a result of the introduction of oil into an initially water-wet system. Initially, small polar species migrate to the initially water-wet mineral surface, giving the surface a more hydrophobic character. Subsequently, the rest of the water phase is replaced by more apolar compounds (e.g. petroleum hydrocarbons) adsorbing on and around these polar. Within months, mineral surfaces rapidly become oil wet.

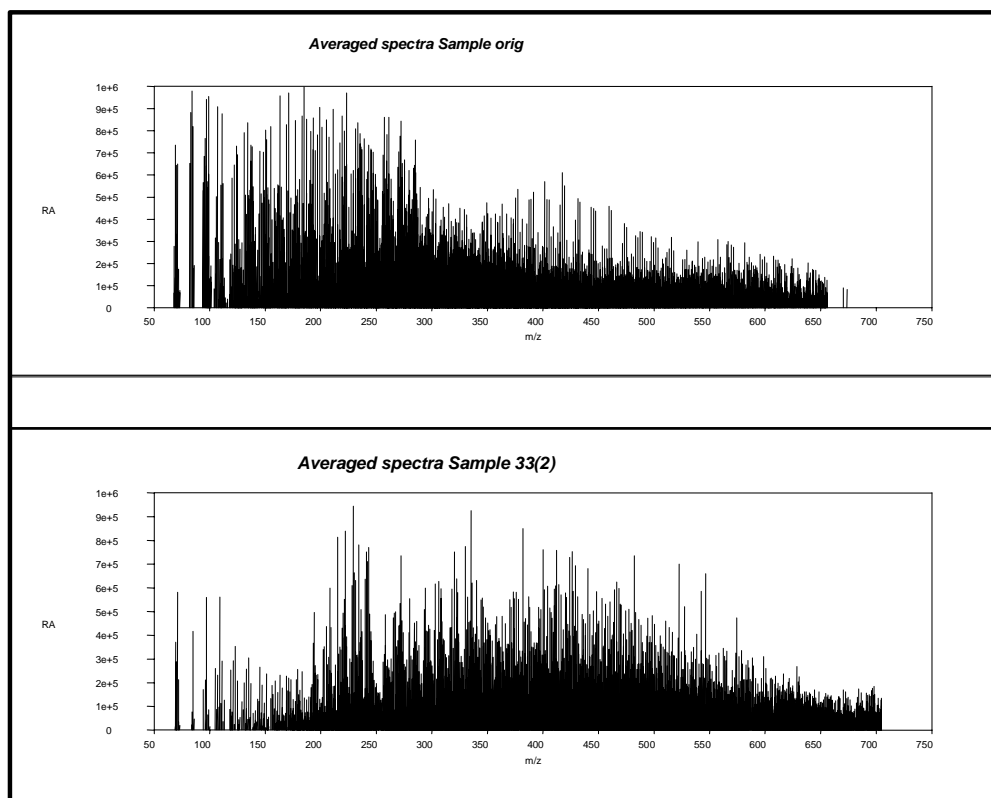


Fig 2. High resolution (38000) low voltage probe mass spectra of a polar compound fraction of a 41 ° API gravity oil (top trace), isolated by solid phase extraction methods (Bennett et al, 1996). The lower trace shows the same oil after passage through a clay rich, initially water saturated, microDarcy permeability siltstone core. The major differences in the traces are at the low molecular weight end of the mixture with much reduction in compounds with less than 250Dalton. These multifunctional surfactant compounds are retained by the core.

## **Summary**

Field studies and core floods of fine grained rocks clearly indicate that polar petroleum compounds are removed from oil onto the mineral surface of fine grained rocks, despite the initial presence of water films. Computational chemistry confirms that low molecular weight polar compounds, of which phenols are probably just one class, readily penetrate mineral water films to change surface properties such that hydrocarbons can wet the mineral surfaces. Examination of siltstone cores flooded with brine, then oil, indicate that sorption of polar compounds appears to correlate with changes from an initial water wet state to a more oil wet state. Oils in contact with caprocks would partition phenols and other surfactants into caprock waters, potentially altering the wetting state of the caprock pore network state. We conclude that there is reasonable doubt that water-wet caprocks in contact with oil would remain water-wet for very long. We conjecture therefore that caprocks may represent low permeability chokes to petroleum systems rather than capillary seals as typically envisaged.

## **Acknowledgements**

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