

# Investigating LNAPL drop hysteresis; Implications for residualisation and source zone assessment

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## Introduction

- Light non-aqueous phase liquids (LNAPLs) are frequently a source of persistent, difficult to remediate contaminants in aquifers.
- LNAPLs are characterised by their immiscibility with water, a specific gravity less than one and typically high toxicity.
- LNAPLs do not fully drain from porous media, even under high capillary pressures (Figure 1).
- The difference in imbibition and draining in Figure 1 is a consequence of differences in wetting behaviour.

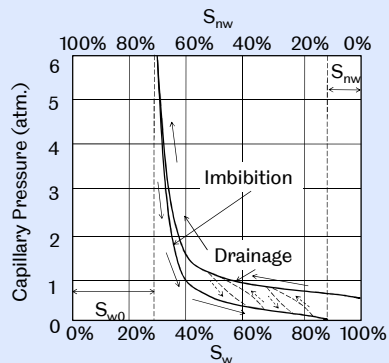


Figure 1 – Idealised capillary pressure/saturation curve for two immiscible fluids in a porous media, showing differences in imbibition and draining saturation states.

## NAPL Wetting

- The process of residualisation ( $S_{nw}$  in Figure 1) is controlled in part by the NAPL wetting characteristics.
- Understanding NAPL wetting behaviour in specific porous media will help in the conceptualisation of a residual NAPL source zone.
- Understanding of source zone wetting characteristics will help in the design of remedial schemes such as free phase recovery by water flooding.

## Wetting and Contact Angle

- The most common determinant of wetting is through the measurement of a static drop contact angle on a representative surface.
- Static contact angles only provide information on a system that is at equilibrium (i.e. neither imbibing or draining).
- In order to employ contact angle as a tool for assessing NAPL residualisation, hysteretic contact angles (advancing and receding) are considered to be superior to static values.

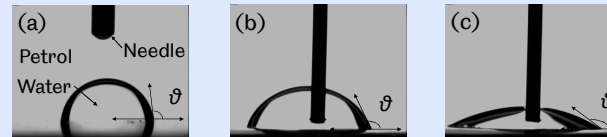


Figure 2 – petrol-water-quartz drop types; (a)-static drop ( $\theta=97.8^\circ$ ), (b)-dynamic advancing drop ( $\theta=103^\circ$ ), (c)-dynamic receding drop ( $\theta=156.8^\circ$ )

- The drop examples shown in Figure 2 can be considered as analogous to a water flood scenario (b) and water drainage by petrol invasion (c).

## Results

- Experimental work has demonstrated that significant variation exists between advancing and receding contact angles both on and between a variety of mineral surfaces studied (Table 1).

Mineral phase	Static contact angle ( $\theta$ )	Max. advancing angle ( $\theta_a$ )	Min. receding angle ( $\theta_r$ )
Quartz	98°	103°	157°
Haematite	94°	86°	128°
Calcite	71°	66°	134°

Table 1 – Petrol-water contact angles recorded in static and dynamic drop experiments (petrol is bulk liquid phase)

## Implications

- Contact angle should be evaluated with respect to variation in mineralogy of porous media.
- The measurement of significant contact angle hysteresis questions the value of static contact angle measurements.
- In order to increase the accuracy of site conceptualisation and risk assessment, or the design efficiency of NAPL source zone remediation, wetting behaviour should be investigated.
- Contact angle should be considered as a dynamic variable and should be measured as such.

## Summary

- NAPL wetting behaviour acts as a control on residual formation.
- Wetting is commonly measured by static contact angle.
- Hysteresis between advancing (invading) and receding (draining) drops can be significant, with the degree of hysteresis varying between mineral surfaces

## Future work

- Possible future work includes;
  - Investigating the effect of altering surface charge on LNAPL contact angle to improve free product recovery and reduce the percentage of residualised NAPL volume.
  - Bench scale core saturation-drainage work to assess mineralogical affects on residualisation in aquifer samples

## References

- Pinder, George, F & Gray, William, G. *Essentials of Multiphase Flow and Transport in Porous Media*. 257pp, John Wiley and Sons, Inc., New Jersey, 2008