Non-Aqueous Phase Liquids („Oil"): NAPL

1.   (D)NAPL INFILRATION AND SPREADING

Severe local groundwater contaminations are often due to the infiltration of liquids such as waste water but also "oils" so-called non-aqueous phase liquids (NAPL), which may be lighter than water (LNAPL: many fuels) or denser than water (DNAPL: chlorinated solvents or coal tars). The former float on the groundwater table while the latter are "sinkers" which means they can infiltrate deep into aquifers and ofter form severe and long-term groundwater contaminations.

1.1   ENTRY PRESSURES - INFILTRATION

For a dense non-aqueous phase liquid (DNAPL) ("oil or organic phase") to infiltrate into an aquifer, it has to displace the water. For this to occur, a certain pressure buildup is needed, which is similar to blowing air into water using a straw.
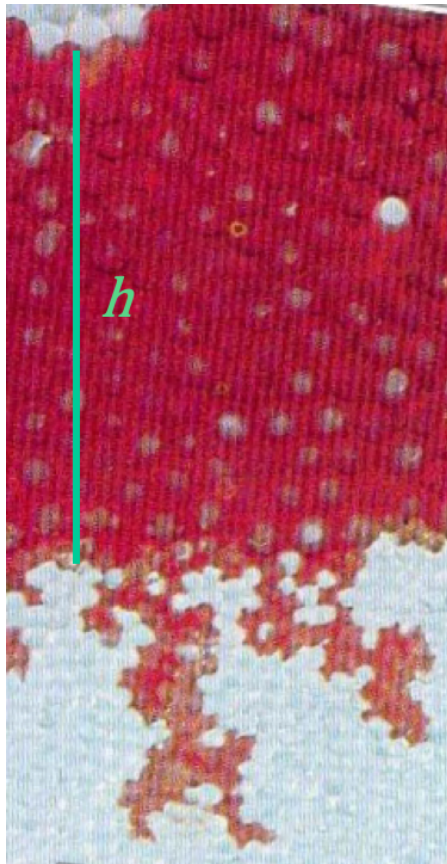

Fig. 1.1: A dense non-aqueous phase liquid (DNAPL) (per-chloroethene (PCE), dyed red) infiltrates into a water-saturated porous media (aquifer made of glass beads, light blue; from Schwille, 1984); the DNAPL accumulates in the coarse layer overlying the fine-grained layer until enough hydrostatic pressure (P_{NAPL}) is built up by the DNAPL (at a height h) to overcome the capillary pressure in the fine material (P_c). At this point, the DNAPL starts to displace the water downwards; here two ganglia form and infiltrate the fine-grained layer (the downwards force overcomes the upwards force):

$$\downarrow P_{NAPL} = h\, g\, (\Delta \rho)$$

$$\uparrow P_c = \frac{2\, \sigma \cos(\theta)}{r_m}$$

g denotes gravity (= 9.81 m s^{-2} or N kg^{-1}) and $\Delta\rho$ is the density difference between DNAPL and water; σ denotes interfacial tension given as force per length [N m^{-1} = kg m s^{-2} m^{-1} = kg s^{-2}] or energy per area [J m^{-2} = N m m^{-2} = kg s^{-2}]. r_m represents the meniscus radius of the interface between NAPL and water in a pore. If water is perfectly wetting ($\theta = 0$; cos(θ) = 1) then r_m corresponds to the capillary radius.

The above is an idealized case; reality, of course, is more complicated than this, but this simple hydrostatic – capillary force balance gives a good idea about the spreading of DNAPLs in porous media. Uncertainties mostly come from unknown meniscus radii (r_m) and wetting angles (θ) in real-world porous media. In the shallow, moist subsurface θ usually is zero (cos (0) = 1).

1.2   GRAVITY DRIVEN SPREADING / INFILTRATION

DNAPLs tend to form pools that spread if they encounter a low permeability layer until the capillary pressure of the underlayer is exceeded (and then they infiltrate). Lateral spreading continues as long as the capillary pressure in the porous medium (host) is exceeded.
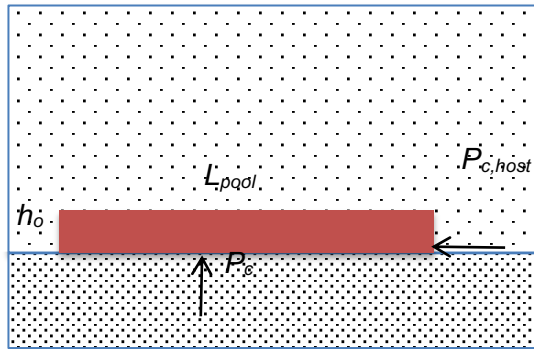
Fig. 1.2: The pressure at the bottom of a DNPL pool (P) is given by its height h_o:

$$P = h_o \, \Delta\rho \, g \left[\text{m} \, \frac{\text{kg}}{\text{m}^3} \, \frac{\text{m}}{\text{s}^2} = \frac{\text{kg}}{\text{m}^2} \, \frac{\text{m}}{\text{s}^2} = \frac{\text{N}}{\text{m}^2} \right]$$

$\Delta\rho$ denotes the density difference between DNAPL and water [kg m^{-3}] (or air in the usaturated zone); below the water table, it is necessary to account for buoyancy forces $= \rho_o - \rho_w$; g is the standard gravity (= 9.81 m s^{-2} or N kg^{-1}).

Thus vertical or lateral migration (or spreading) of the DNAPL pool is possible if the pressure of the DNAPL overcomes the capillary pressure P_c:

$$h_o \, \Delta\rho \, g > P_c = \frac{2\,\sigma}{r_m} \tag{1.1}$$

Eq. 1 describes the height of an organic phase (h_o) above which mobilization occurs:

$$h_o = \frac{P_c}{\Delta\rho \, g} = \frac{2\,\sigma}{r_m \Delta\rho \, g} \tag{1.2}$$

This can be extended to the mobilization of a pool on an inclined layer with angle α:
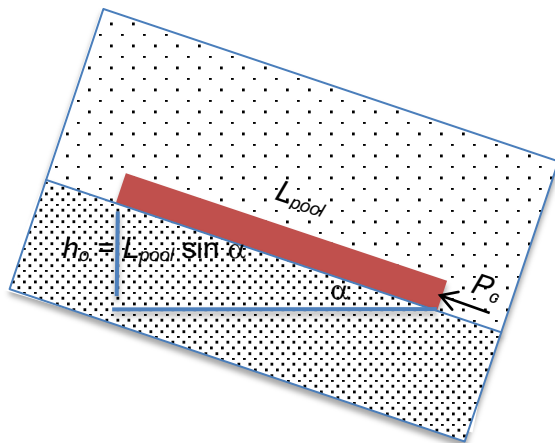
Fig. 1.3: DNPL pool on an inclined layer with angle α

The pool gets mobilized above a critical length (L_{pool}) depending on the angle α of the inclination:

$$L_{pool} = \frac{P_c}{\Delta\rho \, g \, \sin\alpha} = \frac{2\,\sigma}{r_m \, \Delta\rho \, g \, \sin\alpha} \tag{1.3}$$

The height of the pool (typically much smaller than the length) is neglected in eq. 1.3. If α is 90°, Eq. 1.3 equals Eq. 1.1. We can extend that to the vertical mobilization of a single NAPL droplet in a pore by introducing a characteristic length r representing the radius of the droplet (2 $r = L_{pool} = h_o$) and r_m.
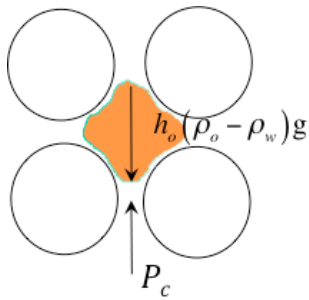
Fig. 1.4: Vertical forces on a DNAPL droplet ("blob") leading to the Bond number for vertical mobilsation; see also Fig. 1.1 and 1.2

This leads to the bond number (Wilfrid Noel Bond, 1897 - 1937), which is the ratio between gravity and capillary forces.

$$N_b \approx \frac{r^2\,\Delta\rho\,g}{\sigma}\ \approx\ \frac{K_i\,\Delta\rho\,g}{\sigma} \tag{1.4}$$

K_i denotes the intrinsic permeability [m²], which is a function of the pore size squared (r^2). At large Bond numbers (> 1), gravitation dominates, whereas, at small bond numbers, capillary forces (interfacial tension) dominate. In sand with K_i ca. 10^{-10} m², a density difference of 500 kg m⁻³ and a surface tension of 0.05 N m⁻¹ (or kg s⁻²) N_b would be quite low (10^{-5}) and DNAPL droplets would not get mobile.

2. 　　　MOBILZATION OF NAPL

2.1 　　　MOBILIZATION BY A HYDRAULIC GRADIENT

If a strong hydraulic gradient develops over the length of a DNAPL pool, the hydraulic pressure upgradient of the pool is higher than downgradient, and finally, the pool could be mobilized. This risk may be encountered close to groundwater withdrawal wells.
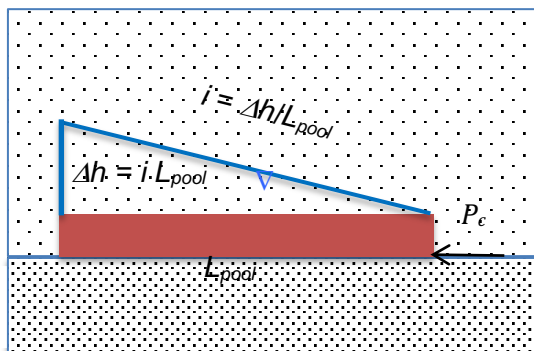

Fig. 2.1: The pressure exerted by a hydraulic gradient over the length of a DNPL is given by:

$$\Delta h\,\rho_w\,g = L_{pool}\,i\,\rho_w\,g\ \left[m\,\frac{kg}{m^3}\,\frac{m}{s^2} = \frac{kg}{m^2}\,\frac{m}{s^2} = \frac{N}{m^2} \right]$$

ρ_w denotes the density of water [kg m⁻³]; g is the standard gravity (= 9.81 m s⁻² or N kg⁻¹).

Mobilization of the DNAPL pool is possible if the hydraulic pressure overcomes the capillary pressure P_c:

$$\Delta h\,\rho_w\,g = L_{pool}\,i\,\rho_w\,g > P_c = \frac{2\sigma}{r_m} \tag{2.1}$$

Thus, the hydraulic gradient above which mobilization occurs is:

$$i = \frac{P_c}{L_{pool}\,\rho_w\,g\,r_m} = \frac{2\,\sigma}{L_{pool}\,\rho_w\,g\,r_m} \tag{2.2}$$

The length of a pool (or ganglion) which becomes mobile at a specific gradient i or flow velocity is (see also Mercer and Cohen, 1990):

$$L_{pool} = \frac{2\,\sigma}{i\,\rho_w\,g\,r_m} = \frac{2\,\sigma\,K}{q\,\rho_w\,g\,r_m} = \frac{2\,\sigma\,K_i}{\eta\,q\,r_m} \tag{2.3}$$

K_i [m²], the intrinsic permeability is related to the hydraulic conductivity K [m s⁻¹]: $K = K_i\,\rho_w\,g/\eta$; η is the dynamic viscosity of water [kg m⁻¹ s⁻¹ = Pa s], η/ρ_w represents the kinematic viscosity (μ) typically around 1×10^{-6} [m² s⁻¹] (thus η is around 1000 Pa s); q is the Darcy velocity (= $K\,i$). This can be extended to the mobilization of NAPL droplets or ganglia by a hydraulic gradient by replacing L_{pool} by $L_{ganglia}/r_m \times r_m$, which represents a characteristic length ($L_{ganglia}/r_m$ is a dimensionless number). Mobilization of ganglia or droplets starts if the hydrostatic pressure is larger than the capillary pressure:

$$\frac{r_m^2\,L_{ganglia}/r_m\,i\,\rho_w\,g}{2\,\sigma} > 1 \ \ \text{or} \ \ \frac{r_m^2\,i\,\rho_w\,g}{2\,\sigma} > \frac{r_m}{L_{ganglia}} \tag{2.4}$$

This leads to the capillary number, which is the ratio of viscous to capillary forces (Abriola et al., 2012):

$$\frac{r_m^2\,i\,\rho_w\,g}{\sigma} \approx \frac{K_i\,i\,\rho_w\,g}{\sigma} = \frac{K\,i\,\eta}{\sigma} = \frac{q\,\eta}{\sigma} = N_c \tag{2.5}$$
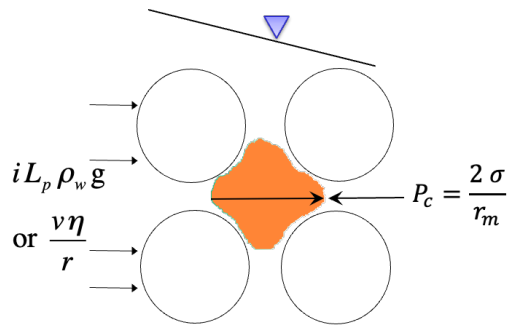

Fig. 2.2: Lateral forces on a DNAPL droplet ("blob") leading to the capillary number for lateral mobilsation; see also Fig. 2.1

According to eq. 2.4, N_c may also be interpreted as a ratio of r_m to $L_{ganglia}$ (much smaller than 1). This approximation comes from the realization that the permeability (K_i) is a function of r^2. According to Leverett, r_m^2 is replaced by K/n (n is the porosity), resulting in a slightly different definition: $N_c = q/n\ \eta/\sigma = v_a\ \eta/\sigma$ (Bergslien and Fountain, 2006; Stöhr and Khalili, 2006); v_a denotes the average flow velocity (= $q/n = K\,i\,/n$). If N_c is larger than 2×10^{-5}, single NAPL blobs will start to get mobilized. If $N_c > 1.3\times10^{-3}$, then complete mobilization can be expected. Since the viscosity of water at 10°C is 1.3×10^{-3} Pa s and the interfacial tension of typical DNAPLs such as chlorinated solvents is around 0.03 N m⁻¹ (= kg s⁻²), then mobilization of DNAPL is not expected even at a groundwater flow velocity of 10 m d⁻¹ (1.2×10^{-4} m s⁻¹) because N_c even at this high flow velocity amounts only to 5×10^{-6}. Note, the capillary number is empirical and based on experimental observations; to estimate it from grain sizes (or the "unknown" meniscus radii) is uncertain, e.g., following Hubbert (1953) the meniscus radius is approx. 1/8 of the grain diameter (d). Using the Kozeny-Carman relationship to estimate the permeability in Leverett's empirical relationship, r_m:

$$r_m \approx \sqrt{\frac{K_i}{n}} \approx \sqrt{\frac{\dfrac{n^3}{5\,(1-n)^2}\dfrac{d^2}{36}}{n}} = \sqrt{\frac{n^2}{180\,(1-n)^2}\,d^2} \tag{2.6}$$

Note, the number 5 denotes the Kozeny-Carman constant (Xu and Yu, 2008), and 36 arises from the specific surface area of a sphere (= $d/6$). For a porosity of 40% or 35%, we get for the meniscus

radius $d/20$ and $d/25$. If K_i [m²] is calculated from the hydraulic conductivity ($K_i = K \eta / (\rho_w g)$) e.g. based on Hazen's relationship ($K_i = 0.0116 \, d^2_{10}$; d^2_{10} is the grain diameter of the 10% fine fraction in mm), then $d/17$ is obtained for a porosity of 35%.

2.2   MOBILIZATION OF NAPL BY SURFACTANTS

Mobilzation of NAPL by surfactants is a technique often applied in enhanced oil recovery but it is also applied occasionally in source zone remediation. If the surfactant concentration in water exceeds the critical micelle concentration (CMC), the interfacial tension is dramatically reduced (see Box 2.1) leading to mobilization of pools and residual NAPL. At the same time the solubility of NAPL constituents is increased which accelerates dissolution kinetics as discussed in next chapter.

**Box 2.1: What happens at the critical micelle concentration (CMC)?**

If the concentration of a surfactant in water increases, the interfacial tension decreases slowly, but as the CMC is exceeded it drops dramatically. With micelles forming the solubility of hydrophobic organic compounds starts to increase. At the same time detergency (cleansing quality/power) increases rapidly.

Fig. 1. Physical property curves for sodium dodecyl sulfate.   Temperature = 25-38°C.
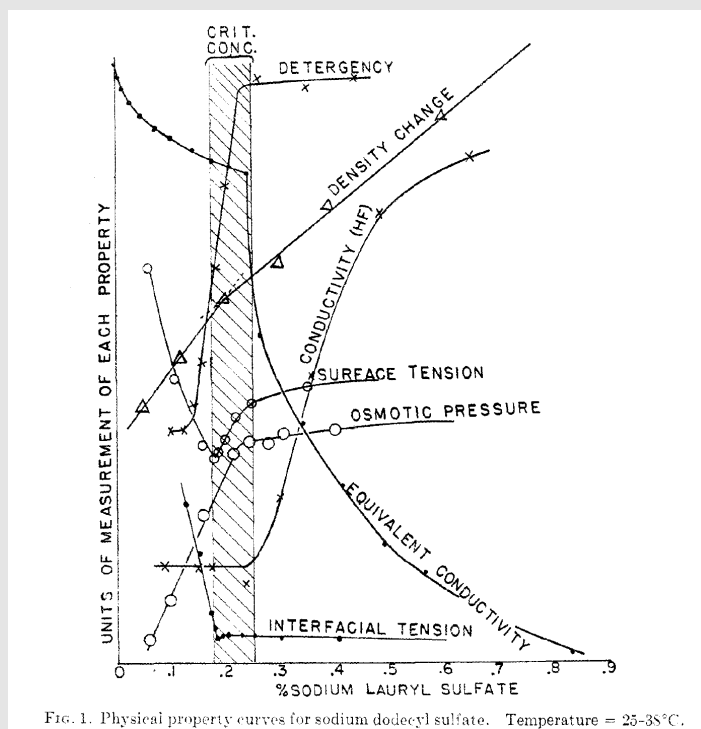
Preston, W. C. 1948. Some correlating principles of surfactant action.

J. Phys. Colloid Chem., 52, 84–96

In microemulsions (e.g., in water / oil / salt mixtures) a so-called middle phases form with ultra-low interfacial tension forms. This effect was originally used for enhanced oil recovery but was also proposed to the remediation of NAPL contaminated sites. Since such systems are hard to control in the subsurface environment and require large amounts of chemicals, this remediation technology is hardly applied anymore.
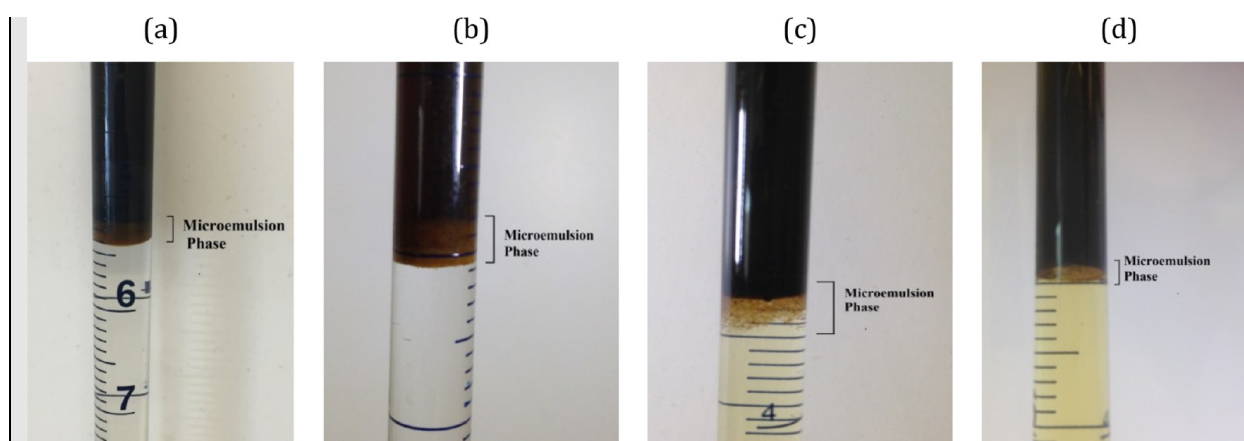
Winsor type III microemulsion phase between NAPL and 0.2 wt % surfactant solution in brine:

(a) n-dodecyl β-D-maltoside, (b) biosoft N1-7, (c) Triton X-100, and (d) Saponin

From: Javanbakht, G., Goual, L. 2016. Impact of Surfactant Structure on NAPL Mobilization and Solubilization in Porous Media. Ind. Eng. Chem. Res. 55, 11736–11746, DOI: 10.1021/acs.iecr.6b03006

3.   RESIDUAL SATURATION AND PERMEABILITY

3.1   (D)NAPL: RESIDUAL SATURATION AND HYSTERESIS

When a non-aqueous phase liquid (NAPL) ("oil") infiltrates into a water-saturated porous media, it will displace the pore water. If hydraulic pressures increase, water from smaller pores is drained by the non-wetting phase (here NAPL), but finally, some residual water is left over. If the process is reversed by infiltration of water, the non-wetting phase is removed, but again not everything can be removed, and some residual phase is leftover (Fig. 3.1). This could correspond to a scenario where a light nonaqueous phase liquid (LNAPL), less dense than water, accumulated at the groundwater table, which seasonally fluctuates, creating trapped LNAPL in the fluctuation zone (a "smear zone" or residual LNAPL).
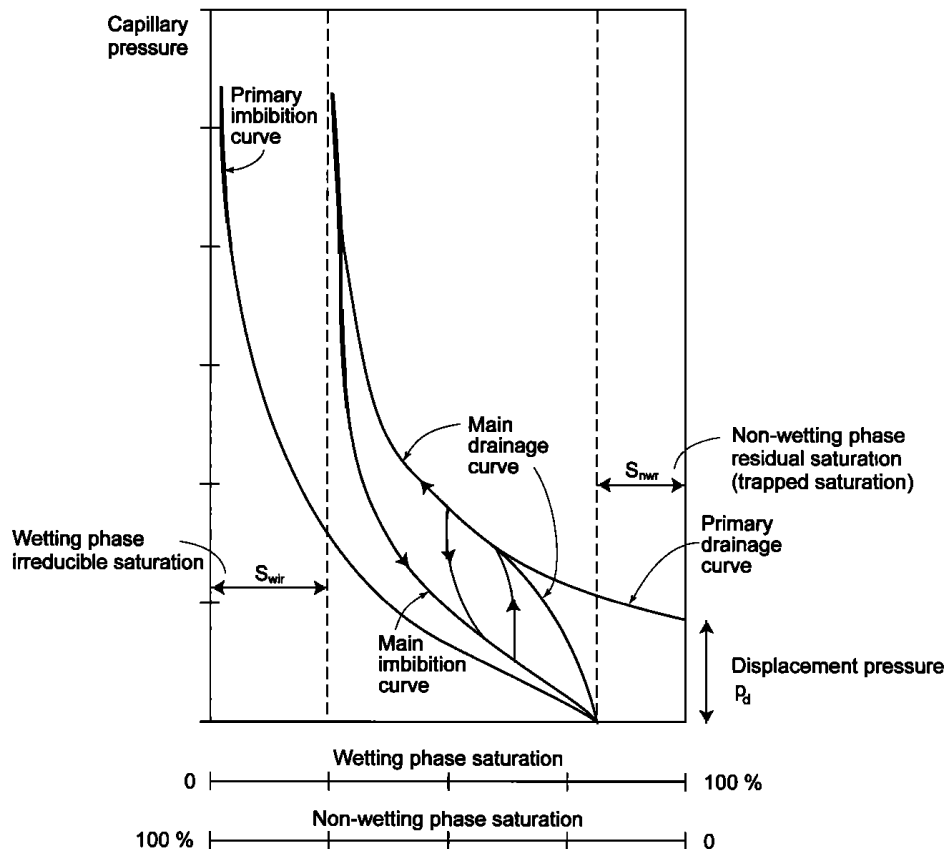
Fig. 3.1: Drainage of water after a non-wetting phase (e.g., NAPL). As NAPL overcomes the displacement pressure (starting from the right: primary drainage curve) water drains from smaller and smaller pores (at increasing capillary pressure), but some water is left as residual phase (irreducible water saturation). When the porous medium is flooded again with water (main imbibition curve), then NAPL is displaced, but again some residual phase is left over (the primary imbibition curve starts in NAPL saturated system and is just the opposite of the primary drainage curve.

3.2   RELATIVE PERMEABILITY

If a porous medium is not saturated with just one fluid, but contains two fluids, then the flow of both are hindered, leading to reduced permeability. Therefore, the flow of groundwater in a "smear zone" containing residual LNAPL is slower than in the surrounding oil-free aquifer – the water flows around the smear zone. This is described by relative permeability curves, as shown in Fig. 3.2.
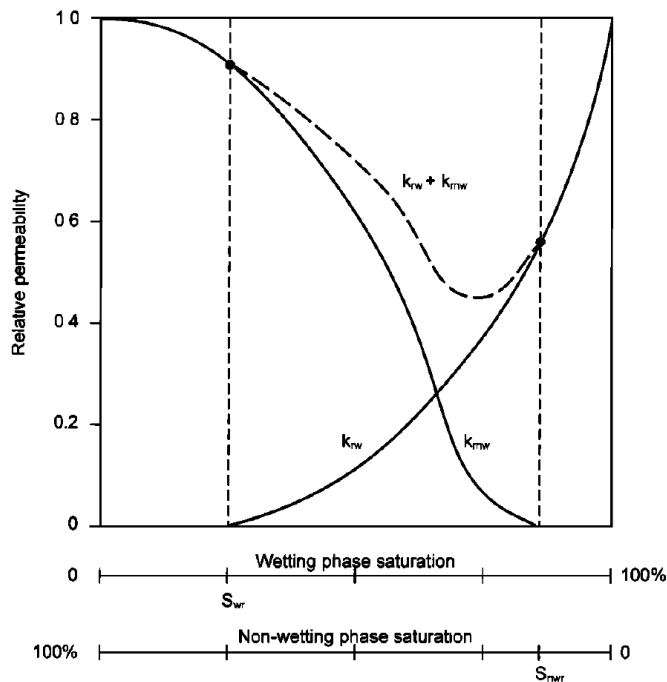
Fig. 3.2: Relative permeability (k_r) of the wetting phase (k_{rw}, starting upper right corner) decreases with decreasing saturation until residual saturation is reached (S_{wr}); starting from the left the same for the nonwetting phase. From Mayer and Hassanizadeh (2005).

4.   REFERENCES

Recommended readings in bold

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