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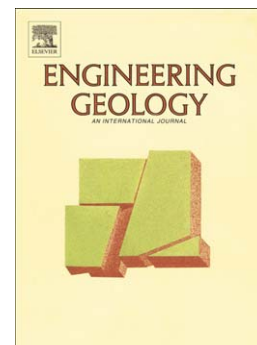
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Response to ENGE07253 Discussion of: "Predicting water permeability in sedimentary rocks from capillary imbibition and pore structure" by D. Benavente et al., Engineering Geology (2015) [doi: 10.1016/j.enggeo.2015.06.003]

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Introduction

The authors would like to express their thanks to C. Hall and A. Hamilton for their interest, clarifications and suggestions about our paper, mainly in the analysis of wettability effects on capillary imbibition. They theoretically supported the permeability, porosity and capillary imbibition relations and elegantly demonstrated some of the empirical equations obtained in our paper. They also proposed using low surface-tension liquids to avoid wettability effects on permeability estimations. This discussion is an excellent opportunity to present additional comments and results and to clarify certain aspects of our paper that may not have been clear enough. Thus, we here highlight that our scaling relations assume that rocks present a homogenous porous medium and the saturation state of the wetted zone in capillary imbibition test is the same as the saturation state in the saturated permeability test. As Hall and Hamilton's Discussion points out this is not generally true since the mean liquid content of the wetted zone in imbibition is below saturation as a result of air-trapping.

Theoretical considerations

Hall and Hamilton's Discussion summarises the relationship between sorptivity, which depends on the microstructure and on the physical properties of the liquid phase, and permeability in porous materials. Intrinsic sorptivity, S_* , which is independent of the liquid properties, is related to sorptivity, S , as:

$$S = S_*(\beta\gamma_L/\eta_L)^{1/2} \quad (1)$$

where γ_L is the liquid-air surface tension, η_L is the viscosity of the liquid and β is the wetting index. Hall and Hamilton's Discussion also describes a detailed scaling relation between intrinsic sorptivity, porosity, ϕ , and permeability, k , as follows:

$$k \sim S_*^4 \phi^{-3}, \quad (2)$$

The wetting index is derived from the Young-Laplace's equation (or sometimes referred as Young's or Laplace's equation). For partially wetting liquids, the average radius of curvature, R , of the liquid surface is increased by a factor $1/\beta$, where β fluctuates between 0 and 1 ($0 \leq \beta \leq 1$) (e.g. Taylor et al., 2000; Hall and Hoff, 2012). According to Young-Laplace's equation, the capillary pressure, Δp , can be expressed as:

$$\Delta p = \frac{2\gamma_L}{R}, \quad (3)$$

Eq. (3) can be easily written for capillary tubes as follows:

$$\Delta p = \frac{2\gamma_L \cos\theta}{r}, \quad (4)$$

where γ_L is the liquid-air surface tension, θ is the contact angle and r the tube radius. In this particular case, we can conclude that $\beta \sim \cos\theta$. Similar conclusions can be also found in Ioannou et al. (2004) where β is interpreted as the ratio between solid-air, γ_{SA} , solid-liquid interfacial, γ_{SL} and liquid-air surface tensions $(\gamma_{SA}-\gamma_{SL})/\gamma_L$ (which matches with the definition of $\cos\theta$). In a real pore, the definition of the curvature radius is a hard task and includes characteristics of both pore shape and liquid-solid wetting. As Hall and Hamilton's Discussion points out, wetting index varies considerably from rock to rock, and no doubt depends as much on the sample history as on the mineralogy. It depends on the liquid-solid surface interaction that includes contamination and chemical composition of mineral surface as well as pore shape. In order to avoid the wettability effects, Hall and Hamilton's Discussion suggests using intrinsic sorptivity, that includes the wetting index, rather than sorptivity or the capillary coefficient, C , of water. Capillary coefficient and sorptivity are related by the liquid density at a given temperature, ρ , as $S=C/\rho$.

Benavente et al. (2015) derived a simple equation for predicting permeability as follows:

$$k = C^2 \frac{\eta r}{4\phi \rho^2 \gamma_L \cos\theta}, \quad (5)$$

Eq. (5) includes information on water motion kinetics (capillary coefficient or water absorption coefficient by capillarity, C), water properties (density, ρ , and viscosity, η_L), wetting (interfacial tension, γ_L and contact angle, θ) and pore structure (pore radius, r and porosity, ϕ). This equation considers that the rock is comprised of n parallel capillary tubes and the net pressure driving force is calculated from the capillary pressures according to Young-Laplace's. Eq. (5) can be expressed in terms of intrinsic sorptivity, considering $C = \rho S$, $\beta = \cos\theta$ and inserting Eq. (1) into Eq. (5), i.e.:

$$k = \frac{S_*^2 r}{4\phi}. \quad (6)$$

Estimation of rock wettability

The characterisation of rock wettability was not originally considered in our article, since it was beyond the scope of this study. However, the present discussion opens an important opportunity to provide an advance of the understanding of wettability and its relation to unsaturated and saturated media through the preliminary analysis of such investigation. Hall and Hamilton's Discussion suggests the estimation of permeability k from S_* via Eq. (2) and then to eliminate the effect of the partial wetting. They propose using a low surface-tension liquid (n-decane) to reach the complete wetting of rocks. However, our experience in this field highlights that an accurate characterisation requests the use of several organic liquids at different temperatures (an accurate, although unfortunately hard and time consuming experimental procedure).

Here we present the complete wettability characterisation that we previously performed of four representative rocks studied in Benavente et al. (2015): C3, T12, T13 and T14. They are constituted by different mineralogical and texture characteristics. C3 contains calcite (70%), quartz (25%) and dolomite (5%) grains (Benavente, 2003); calcite is the main mineral in T12 and T13; and T14 is mainly constituted by calcite, although its banded structure defines some non-touching pores and iron minerals are located on the pore surface.

Capillary absorption properties of these rocks were determined using water and hydrocarbons in a range of different temperatures. Water experiments were performed at 15, 20, 25 and 35 °C; ethanol at 20 and 25 °C; and methanol and n-dodecane at 25 °C. The characterisation was carried out in the same samples that were used in Benavente et al. (2015). For each rock and for all liquids at different temperatures, capillary coefficient is obtained and the sorptivity is calculated as $S=C/\rho$.

In Figure 1, sorptivities are plotted versus $(\gamma_L/\eta)^{1/2}$ and two groups can be distinguished, which lie on separate straight lines: on the one side, the group defined by the sorptivities measured with the pure organic liquids and on the other these measured with water. Both straight lines have different slopes. For water, the slopes are lower than for the organic liquids, which indicates the partial wetting of water. The complete wetting is assumed in low surface tension organic liquids and, therefore, with a wetting index $\beta=1$. Intrinsic sorptivities are obtained from

the slope of the straight line obtained with the measures performed with the organic liquids. Wetting index is calculated according to Eq. (1) and using the measures developed with water (see details in Taylor et al., 2000; Hall and Hoff, 2012; Ioannou et al., 2004).

Table 1 shows the water capillary coefficient at 25°C, intrinsic sorptivity and wetting index for the studied rocks. Open porosity and water permeability were performed according to Benavente et al., (2015) experimental procedures.

The intrinsic sorptivity and wetting index values are in concordance with other rocks with similar mineralogical composition (Hall and Hoff, 2012; Ioannou et al., 2004). The studied rocks present a partial wetting and β is influenced by the calcite content and likely by its pore surface contamination. Taylor et al., (2000) noted that the natural contamination strongly modifies the natural hydrophilic character of calcite by reducing the affinity of its surface for water, inducing a hydrophobic state. Thus, the T12 and T13 exhibit the lowest wetting indexes and are constituted mainly by calcite. C3 has ~25% of quartz grains and T14 displays banded structures, where iron oxides and oxyhydroxides cover calcite crystals on the surface of some pores (Garcia-del-Cura et al., 2008; Benavente et al., 2015).

In the previous section, we concluded that Eqs. (2) and (6) avoided the wettability effects in the water permeability estimation. On the one side, Eq. (2) is plotted in Figure 2 and highlights the correlation between k and $S_*^4 \phi^{-3}$. This highly supports the scaling correlations proposed in the Hall and Hamilton's Discussion. On the other, the agreement between experimental and predicted permeability is also promising when using Eq. (6). Considering the threshold pore radius, the volume of pores larger than the threshold pore radius and the effective porosity of Table 2 in Benavente et al., (2015), the predicted permeability values obtained with Eq. (6) for C3, T12, T13 and T14 are respectively 2.49, 0.16, 0.01 and 0.10 mD. Eqs. (2) and (6) assume implicitly that a homogeneous porous media and the state of saturation of the wetted zone in capillary imbibition is the same as that achieved in a saturated permeability test.

Results show that further research into this important topic is needed, particularly by increasing the number and range of rock types and paying special attention into the nature of the minerals at the fluid-solid interface, surface roughness and pore shape, which all can have a strong influence on the wettability.

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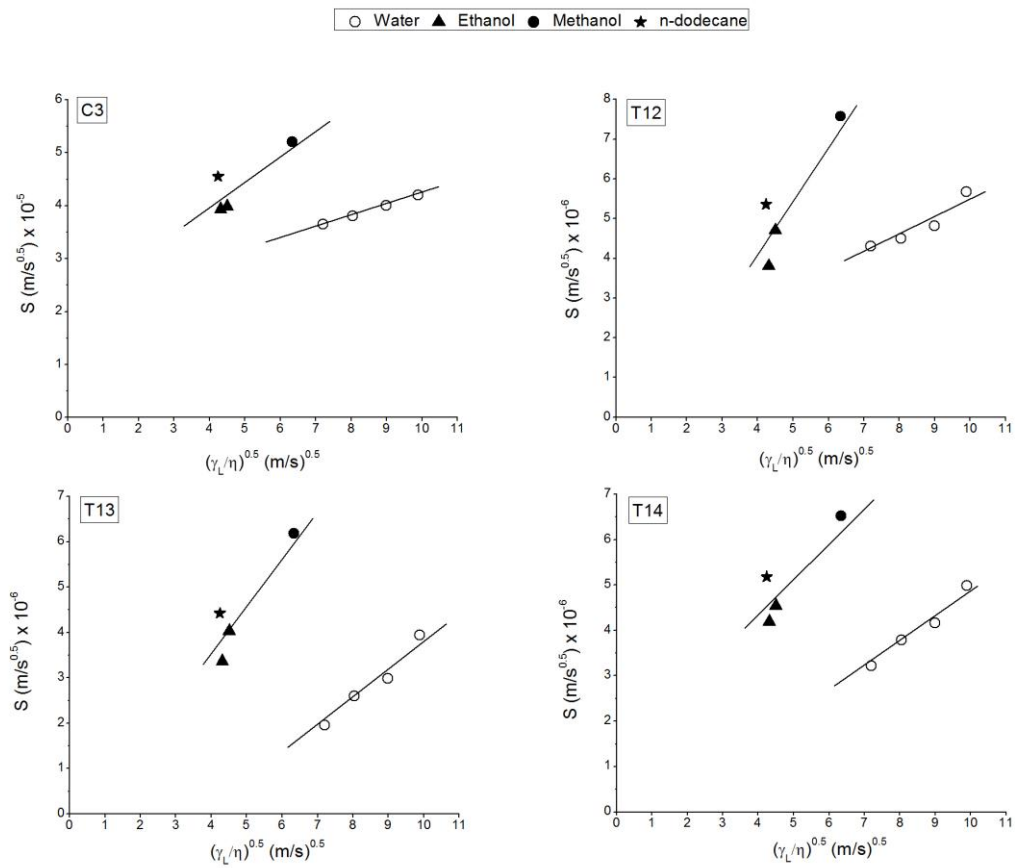


Figure 1. Sorptivity S versus $(\gamma/\eta)^{1/2}$ graphs for water (15, 20, 25 and 35 °C), ethanol (20 and 25 °C), methanol (25 °C) and n-dodecane (25 °C) absorption into studied rocks.

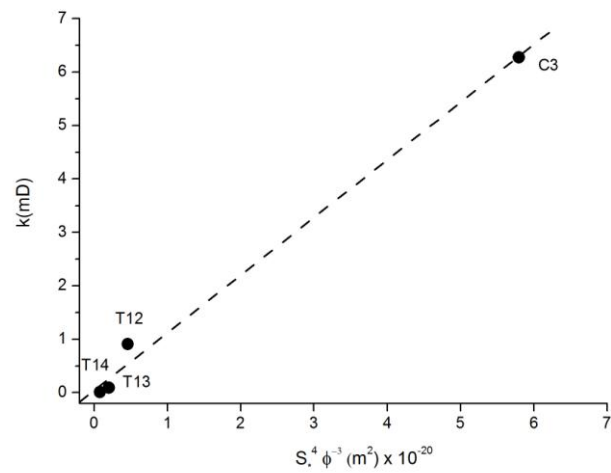


Figure 2. Water permeability versus $S_*^4 \phi^{-3}$ graph for the four studied rocks

Table 1. Capillary coefficient, open porosity, water permeability, intrinsic sorptivity and wetting index for the studied rocks at 25 °C.

	C3	T12	T13	T14
Capillary coefficient, C ($\text{g}/\text{m}^2\text{s}^{0.5}$)	39.83	4.81	2.94	4.15
Open porosity, ϕ (%)	22.03	6.19	7.09	12.54
Water permeability, k (m^2)	6.27	0.91	0.007	0.093
Intrinsic sorptivity, S_* ($\text{m}^{0.5}$)	$4.99 \cdot 10^{-6}$	$1.46 \cdot 10^{-6}$	$1.11 \cdot 10^{-6}$	$9.16 \cdot 10^{-7}$
Wetting index, β	0.38	0.14	0.20	0.33

Highlights

Intrinsic sorptivity is used to predict water permeability

Partial wetting of water is obtained in calcitic sedimentary rocks

Relations relating permeability, imbibition, sorptivity, porosity and pore size are discussed