Water-entry pressure in water repellent soils: a review

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Abstract. Water repellent soils can be naturally promoted (e.g. after wildfires) or synthetically induced by mixing with hydrophobic compounds (e.g. polydimethylsiloxane). The study of soil water repellency has lasted for over one century which implied the significant effect of soil water repellency on water infiltration, evaporation, soil strength, and soil stability. Water repellent soils can also be exploited by geotechnical engineers to offer novel and economical solutions for ground infrastructure. This paper synthesizes different methods for assessing soil water repellency based on varied indexes (e.g. contact angle, time for a drop to infiltrate) and with a focus on water entry pressure. Measurements of these parameters in synthetic water-repellent sands were taken, some results of which are summarized with discussion of key factors affecting water repellency. A comparison of these methods shows that water entry pressure can be more representative for assessing the water repellency of bulk samples.

1 Introduction

Soil water repellency (or hydrophobicity) has been studied worldwide for over one century [1]. It can be naturally promoted after wildfires from the burning of organic matter or artificially induced from hydrophobizing compounds (e.g. silane compounds and fatty acids) [2-5].

The importance of soil water repellency in geotechnical engineering has been recognized due to its significant effect on water infiltration, evaporation, soil strength, and soil stability [6, 7]. Potential applications of water repellent soils (WRS) in ground infrastructure include hydraulic barriers for embankments, landfills, flood defences and other applications [8-10]. The assessment of water repellency hence becomes essential. The two commonly used methods for characterizing the magnitude of water repellency are contact angle measurement and water drop penetration time test [11]. These methods take advantage of the interaction between liquid and solid, through a balance of capillary forces (Eq. 1).

$$H = 2\gamma \cos\theta / r\rho g \tag{1}$$

Where H is the height of capillary rise; γ is the liquid-air surface tension; θ is the liquid-solid contact angle; r is the equivalent capillary tube radius; ρ is the liquid density; g is the gravitational constant. However, it is challenging to assess the water repellency of a bulk sample by these methods. Water entry pressure represents an alternative method and will be further developed in this paper. The aim of this paper is to review different methods for assessing soil wettability, with a particular focus on water entry pressure. Traditional methods including contact angle

measurement, water drop penetration time, and molarity of ethanol drop will be introduced first. Both underlying theories and methods will be introduced at first including sample results. Water entry pressure test, as a novel method to quantify soil water repellency, will follow.

2 Quantification of water repellency

2.1 Contact angles

The direct expression of surface wettability can be obtained from contact angle measurements, which is one of the most commonly used methods to assess wettability [10-12]. When a droplet of liquid is placed on a flat solid surface, due to the different surface energies of the three phases (i.e. solid, liquid, vapor), it exhibits different shapes. The angle between the three-phase contact lines (i.e. solid-liquid, liquid-vapor, solid-vapor) is hence determined as a contact angle (Fig. 1).



Fig. 1. Definition of contact angle

The contact angle depicts the interaction of the interfacial tensions, indicating the wettability of a liquid drop to a given solid surface. Young (e.g. [3], proposed the equation below (Eq. 2) which describes the relationship between the three interfacial energies.

$$\cos\theta_{Y} = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \tag{2}$$

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Where θ_{γ} is Young's contact angle, γ refers to interfacial energies between different phases. However, this equation is applicable when the solid surface is smooth, flat, homogenous, inert, insoluble, nonreactive, non-porous and non-deformable [13]. Wenzel and Cassie-Baxter models [14-16] considered these factors, and proposed new expressions which can be applicable to porous media such as soils. Wenzel modified Young's model as illustrated in Eq.3 [14-16].

$$\cos\theta_W = r\cos\theta_Y \tag{3}$$

Where θ_W is the Wenzel contact angle, θ_Y is Young's contact angle and r is the roughness index defined as the ratio of the true to the apparent area of the solid surface. The Wenzel model stressed the influence of surface roughness on contact angle; the existence of imperfections on a solid surface results in an enhancement of hydrophobicity if the surface is initially hydrophobic. But hydrophilicity will be enhanced if it is initially hydrophilic, which can be easily derived from Eq.1. For instance, because r must have a value greater than 1 for rough surfaces, larger r results in larger θ_W if $\theta_{\rm Y}$ is greater than 90°. However, Wenzel's model describes a 'wetting state' where liquid fills the grooves completely (Fig. 2a). There are some cases where a liquid does not penetrate into the grooves completely with part of it contacting the air trapped in between these features (Fig. 2b). Cassie's equation can be used in these situations [17].

$$\cos\theta_{C} = f_{1}\cos\theta_{Y1} + f_{2}\cos\theta_{Y2} \tag{4}$$

Where θ_C is the Cassie contact angle, f_1 and f_2 are the fraction areas in contact with phase 1 and phase 2, θ_{YI} and θ_{Y2} are the contact angles between different contacting phases. This equation can be reduced to Cassie-Baxter equation (Eq.5) since the contact angle between water and air is 180°.

$$\cos\theta_C = f_1 \cos\theta_{Y1} - f_2 \tag{5}$$

The combination of Wenzel and Cassie-Baxter models are widely used in practical surfaces which are usually rough and heterogeneous and is also applicable in porous materials such as soils [18].

A plethora of methods has been introduced in the past decades. Some of the methods take advantage of the forces (or work) produced (or done) by liquid surface tension, which is easier to be observed, such as the Wilhelmy plate method and capillary rise method [3, 19]. These methods use the theoretically established relationship between contact angle and surface tension to calculate the contact angle. For soils or other granular materials, the sessile drop method (SDM) [3] has been suggested. By using a double-sided adhesive tape, soil particles can be fixed on a glass slide forming a monolayer structure. A drop of deionized water is then placed on the particles, and images or videos of the droplet motion is recorded by simply using a camera and backlight source. Further analysis can be done with certain programs or in image processing software such as ImageJ to deduce the apparent contact angle (hereinafter named 'CA' for ease of reference) [10, 20]. Table 2 summarized the results of contact angle measurements for Fujian sand treated with 0.5% dimethyldichlorosilane (DMDCS).



Fig. 2. Models describing different wetting state: (a) Wenzel model and (b) Cassie-Baxter model

Fujian sand, also known as Xiamen ISO standard sand, is used in this study. It is silica-based sand and the particles used for tests have been sieved to 3 ranges (mm): 0.063-0.30, 0.60-1.18, 1.18-2.00. The particle characteristics of the sand including its shape and size (Table 1) were obtained by a dynamic image analyzer (QicPic; Sympatec GmbH, Clausthal-Zellerfeld, Germany.)

Table 1. Characteristics of Fujian sand

	63-300µm	600-1180µ m	1180-2000µm
D10	153	766	1217
D50	213	957	1607
D90	316	1235	2080
Sphericity	0.8774	0.8866	0.8834
Aspect ratio	0.7269	0.7537	0.7388
Convexity	0.9211	0.9635	0.9703

The samples are then treated with dimethyldichlorosilane (DMDCS; Acros Organics, New Jersey, USA) to induce water repellency; 0.5% of DMDCS in terms of mass ratio were used. All the treated samples were kept in the open air for 24 hours before any measurement.

Table 2. Contact angles of 0.5%DMDCS treated Fujian sands

Particle size (µm)	Treatment	Contact angle (°)	
63-300		126	
600-1180	0.5% DMDCS	112	
1180-2000		101	

Finer sand exhibits higher apparent contact angle when treated with DMDCS at the same concentration.

2.2 Other methods

Water Drop Penetration Time (WDPT) is the time required for a drop of water to infiltrate soil completely [21]. As Eq. 1 suggests, wettable soils have a positive capillary rise height for water. The water on top replaces air trapped in soil pores causing spontaneous and immediate infiltration. For water-repellent soils, the capillary height has a negative value with water drops able to stand without entering the pores, (the soil is said to be in a Cassie-Baxter state). However, surface tension and contact angle may change with time resulting in a decrease in soil water repellency. The drops start to infiltrate into soil after a period of time [11]. Hence, water drop penetration time, which quantifies the persistence of water repellency, serves as another parameter for assessing soil wettability. The WDPT test requires timing complete infiltration for 6 drops (65 µl for each). To illustrate the effect of the silanization on WDPT, measurements of different sized Fujian sands treated with 0.5% DMDCS have been done, i.e. in the same materials of Table 1, all the WDPTs were greater than 3600s (Table 3) [21]. All tested samples are extremely water repellent according to a classification widely used in soil science [21].

Particle size (µm)	Treatment	WDPT (s)
63-300		
600-1180	0.5% DMDCS	>3600
1180-2000		

The Molarity of an Ethanol Drop (MED) test, also named as alcohol percentage (AP) test, is also commonly used to characterize soil water repellency. The test is conducted by firstly mixing alcohol and water in a series of ratios. The higher ethanol concentration leads to the lower surface tension of the mixture but higher capability of wetting hydrophobic soil. Drops of aqueous ethanol solutions containing increasing ethanol concentrations are placed on soils, with the time of infiltration noted. As the AP and surface tension of the solution that has a five-second infiltration time is recorded, these two parameters reflect soil water repellency. This surface tension is also taken as 90° surface tension (γ_{ND}) as specified by Watson and Letey (1970) and can be combined with Young's equation to derive the initial contact angle [11, 22, 23]. Measurements were also conducted in the same materials of Table 1, with the results illustrated in Table 4. All the tested samples are extremely water repellent.

 Table 4. MED test results of 0.5%DMDCS treated Fujian sands

Particle size (µm)	Treatment	Molarity (mol/L)	γ _{ND} (mN/m)
63-300	0.5% DMDCS	5.7	35.38
600-1180		5.4	36.18
1180-2000		5.3	36.45

3 Water entry pressure

3.1 Breakthrough pressure

Water entry pressure (WEP), also known as water-entry value or breakthrough pressure of water, is defined as the critical pressure at which water starts to infiltrate or breaks through into the soil pores [24]. It has been recognized as an increasingly important parameter to assess soil water repellency as it demonstrates its ability to retard or impede infiltration in a water-repellent soil [25]. The ability of water-repellent soils retarding water can be explained by capillary theory [11, 24, 26, 27]. As mentioned in section 3.2, water-repellent soils have a negative value of capillary rise height (Eq.1) which results from the molecular forces between liquid and solid. For a water-repellent soil, air tends to replace water as it is more wettable to the solid surface than water. Due to the curvature of the water-air interface, a Laplace pressure towards the water is generated and hence stops the water from infiltrating into the pores (Fig. 3). In terms of pressure, the breakthrough pressure can be presented as [19, 24].

$$BP = -2\gamma\cos\theta/r \tag{6}$$



Fig. 3. Sketch of capillary rise within pores of water-repellent soils

For water repellent soils, the value of WEP is positive, while wettable soils have a negative WEP (suction). However, the breakthrough pressure obtained from this equation can only be applied to idealised media, as it assumes all the pores in the soil have the same radius. Therefore, the magnitude of water entry pressure varies with soil properties and state variables [26]. Several studies on these contributing parameters have been carried out for past decades. Next, the different set-ups and results are reviewed and compared.

3.2 Experimental set-ups based on the waterponding method

Mainly two methods have been reported for WEP measurements. The most widely used method is the water-ponding (WP) method. Many variations on the setups using WP have been suggested. The key concept of this method is to directly apply a water head on the soil surface with a pond of water and increase the water head until infiltration occurs. The use of water ponding above the soil surface is simple and effective. Water is

directly added on top of a soil column within a transparent tube (Fig. 4a). The water pressure at soil water interface is recorded once the water starts to get into the soil, which is the WEP of the tested soil. The pressure can be read by means of a pressure transducer or simply calculated from the water head. The onset of infiltration can be recognized by observation of a sudden drop of water head or pressure at soil-water interface. However, the exact time is difficult to capture by visual observation. Therefore, sensors can be installed inside the soil to detect the moisture change and hence, determine the onset of infiltrating. However, Lee et al. 2015 recorded higher values than the true WEP by placing the electrodes at the bottom of the soil. A more accurate WEP can be obtained if the sensors (electrodes) were installed close to (but below) the soil-water interface [11, 28]. WP method is also applicable for insitu measurements by using rings instead of transparent tubes as illustrated in Fig. 4b [25]. Other set-ups are also reported based on the WP method. The use of permeameters and stand-pipes makes it possible to apply the water pressure to the soil radially (Fig. 4c) [29]. Three key points requiring attention for set-ups based on the WP method include: (1) pore air drainage of the soil should be guaranteed; (2) water head should be relatively static (with a low flow rate imposed). The Mariotte's bottle is usually used for controlling flow rate when adding water; (3) the inside wall of the tube (or ring) should be treated with hydrophobic coatings (e.g. Teflon, bentonite) to prevent soil-wall preferential flow or leakage [25, 26, 28].



Fig. 4. Different set-ups based on WP method: (a) water ponding on soil surface; (b) water ponding in the field; (c) water ponding in a stand-pipe (after [25])

3.3 Experimental set-ups based on tensionpressure infiltrometer

Tension-pressure infiltrometer (TPI) was suggested by Wang et al. 2000 to assess the wettability of both wettable and non-wettable soil in terms of WEP [25]. The TPI set-up is modified from the tension infiltrometer which was originally designed for supplying pressures less than or equal to zero [30]. A sketch of the setup is shown in Fig. 5. A Mariotte water reservoir on the lefthand side is connected to a porous disk touching the soil below. As the only air inlet tube is connected to a bubble tower, the outlet water pressure, which is at the soil surface, will be regulated by adjusting the bubble tube height z_1 . When $z_1=z_2$, the pressure at the infiltration surface is zero. When $z_1 < z_2$, a positive water pressure towards soil will be imposed, while for $z_1 > z_2$, negative pressure (suction) will be induced. The test starts with the largest suction (maximum z_1) at the soil surface. By slowly moving the bubble tube upwards (decreasing z_1), a smaller suction will be generated. For wettable soils, once the suction imposed by the TPI is smaller than the suction produced from the soil, water will infiltrate. Hence, the WEP (negative in this case) of the soil can be determined by recording suction at the infiltration onset [25, 30]. For water repellent soils, infiltration will occur when $z_2 > z_1$ and the imposed water pressure larger than its breakthrough pressure, which is similar to WP method.



Fig. 5. WEP measurement using tension infiltrometer

The literature has shown that a higher degree of water repellency and higher density (lower porosity) of a soil results in a larger water entry pressure [11, 26, 28]. Other results include: (1) a negative correlation of temperature and WEP has been reported [29]; (2) rounded particles have a lower WEP [31]; (3) the WEP of dry soil could be affected by soil organic matter and clay content [25].

This paper summarizes various methods for soil water repellency assessment. The contact angle (CA), water drop penetration time (WDPT), and molarity of an ethanol droplet (MED) are all widely used in different fields. CA is the most widely used. However, the limitation of using small droplets creates scale effects when dealing with measurements in irregular surfaces (such as soils) or when there is a need to investigate bulk samples. WDPT takes time into consideration but is not suitable for soil with a high degree of water repellency, because the time for the droplet penetration for these samples might be longer than the time needed for the evaporation of the droplets. MED is suitable for most of the samples and can quantify wettability indirectly through the surface tension. However, the preparation procedure can be lengthy and the results may not find direct application in engineering design (the same for the WDPT). Thus, the water entry pressure (WEP) test represents a suitable alternative. It is advantageous as it accounts for both the soil matrix and state variables and is therefore more suitable for geotechnical design.

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