Effect of wetting and drying on meniscus structures in hydrophobic sands

Zeynep Karatza¹, Jim Buckman², Gabriela M. Medero³, and Christopher T. S. Beckett¹

¹Institute for Infrastructure and the Environment, School of Engineering, The University of Edinburgh, EH9 3JL, UK

²Institute of Geoenergy Engineering, EGIS, Heriot-Watt University, EH14 4AS, UK

³Institute for Infrastructure and the Environment, Energy, Geoscience, Infrastructure and Society, Heriot-Watt University, EH14 4AS, UK

Abstract. Hydrophobic soils can occur either naturally when particles are coated with plant-derived hydrophobic organic compounds or if exposed to very high temperatures, or artificially if treated with contaminated water or chemicals in the laboratory. Hydrophobic soils can resist water infiltration, are associated with preferential flow and may lead to increased surface runoff and soil erosion. Traditional understanding of unsaturated hydrophobic soils suggests that convex water menisci, and so positive water pressures, should form between soil particles, due to contact angles $> 90^\circ$. However, experimental results do not support this theory. The objective of this work was to study the changes in meniscus structures in hydrophobic sand specimens, as well as the overall response of the sand to wetting and drying cycles. A very uniform, fine silica sand was mixed with Dimethyldichlorosilane to induce water repellence. Successive images captured in an environmental scanning electron microscope are presented, to examine the response of the sand in two distinct drying and wetting cycles. Preliminary results show that the non-spherical nature of the sand particles prevent or hinder the formation of convex liquid bridges, despite the high contact angles. Rather, water droplets appear to expand only through droplet coalescence, which prevents structures from contracting on drying.

1 Introduction

Hydrophobic soils naturally form in arid regions when particles are coated with plant oils or if exposed to very high temperatures, for example during forest fires. Soils can also become hydrophobic if treated with contaminated water or chemicals in the laboratory. Water-repellent soils can be problematic as they are often associated with reduction of soil infiltration capacity, preferential flow and may lead to increased surface runoff and soil erosion [1].

In unsaturated soil mechanics the presence of both air and water in the pore space introduces a complexity to the study of the macroscopic behaviour of a soil. Therefore, it is obvious why researchers focus on microstructural experimental studies [e.g. 2] and particle scale constitutive models [e.g. 3, 4] to describe and predict the macroscopic response of unsaturated soils.

The water retention curve is commonly used to evaluate the macroscopic behaviour of unsaturated soils during adsorption (wetting) or desorption (drying) processes [e.g. 5], without considering the effects of volume changes and stress state [6]. Hysteresis between the wetting and drying paths is also commonly interpreted in the absence of volume or pore size distribution changes [7]. However, repeated cycles of drying and wetting can lead to changes in the soil structure through shrinking and swelling [8]. Hence, the water retention curve does not provide a unique relationship between water content and suction [9, 10].

The contact angle forming between a particle and a liquid has been shown to affect the macroscopic water re-

tention behaviour of a soil [11, 12]. Conventional understanding of the particle scale holds that a drop of liquid between two identical, hydrophilic solid spheres will form an axisymmetric, concave liquid bridge to minimize surface energy (assuming that the particles are not in motion) [e.g. 13–16]. The capillary force of the concave liquid bridge acts as a bonding force, attracting the particles together, giving rise to suction (i.e. negative pore water pressure) [17]. There is evidence, however, that above a critical volume of water, the liquid bridge between hydrophilic spheres may adopt an asymmetric, convex shape [18]. According to [19]: ‘*water can be used as a test liquid to establish (via the advancing contact angle, i.e. the contact angle that is measured immediately after the sessile drop is placed on a coated surface) whether a surface is hydrophilic (angle $< 45^\circ$) or hydrophobic (angle $> 90^\circ$)*’. Recent studies have shown that water trapped between hydrophobic surfaces also forms convex capillary bridges between the particles, suggesting that the water acts to force the particles apart (i.e. positive pore water pressure) [17].

Despite the convex shape of the capillary bridges, there has been little evidence in the literature of positive pore water pressure in water retention curves of hydrophobic soils [e.g. 12]. Commonly, positive suction values are measured in both hydrophobised and non-hydrophobised soils; however, the water retention curves present significant differences in shape between the two materials [11, 20, 21]. Recently, Lourenço et. al., [22] suggested that the shape of the meniscus is controlled by the nature

(a) Hydrophilic glass beads at 0.87 kPa P_{H_2O} and 98.7 % RH with concave menisci

(b) Hydrophobic glass beads at 0.87 kPa P_{H_2O} and 98.8 % RH with convex menisci

Figure 1: ESEM images of hydrophilic and hydrophobic spherical glass beads under wetting conditions from an initially dry state ($D_{50} = 97 \mu m$).

of the materials involved, irrespective of the size and shape of the individual particles, and observed coexisting convex and concave menisci forming in a polydisperse sample of spheres.

The uncertainty regarding the mechanisms involved in the formation of convex capillary bridges in hydrophobic soils is the key motivation of this project. The main focus of this paper is to present the start of that work, studying the response to wetting and drying after a number of such cycles, the hysteresis and the changes in the menisci structures in hydrophobic sand specimens.

2 Experimental Campaign

For this study very uniform ($D_{min} = 63 \mu m$ and $D_{max} = 106 \mu m$), silica sand (99.4% SiO_2) and glass bead were used. The glass beads are highly spherical, whereas the sand particles are sub-rounded of medium sphericity. Both particle size limits were chosen according to environmental scanning electron microscopy imaging restrictions.

Water repellence was induced by mixing 1 mL of Dimethyldichlorosilane (DMDCS) with 500 g of dry sand, to form a hydrophobic coating on the soil sample. The ratio of DMDCS to sand was decided based on the average sand particle size, according to [23].

A dry sample of the hydrophobic sand was placed in an environmental scanning electron microscope (ESEM; QUANTA FEG 650; see [24] for details), whilst the partial pressure of water vapour (P_{H_2O}) in the specimen chamber was controlled to investigate the formation and shape of liquid bridges. To achieve a relative humidity (RH) of 100 % for the operating range of the scanner, the temperature of the specimen chamber was reduced to and kept constant at 5 °C. At this temperature the equilibrium vapour pressure is 0.87 kPa.

Each wetting/drying cycle starts from an initial 0.53 kPa P_{H_2O} and 61.3 % RH (no droplets were observed on the particle surfaces due to the low temperature of the chamber), gradually increasing to 0.87 kPa and 100 % respectively, and finally decreasing back to the initial value of P_{H_2O} and RH . The cycle was repeated twice, with a rate of $0.027 \text{ kPa min}^{-1}$, leaving the sample to stabilise for 2 min at the end of each wetting or drying phase (the sufficiency of this time was confirmed visually). Through the psychrometric equation, total suction increases while RH decreases and for $RH = 1$ (i.e. 100%) the total suction is 0 kPa. In this work, however, we will not be assigning specific suction values at different states of RH , as hydrophilicity is implicit in the derivation of the psychrometric equation whilst we are studying hydrophobic soils. This test was performed on glass beads and the silica sand described earlier, for both hydrophobic and hydrophilic states. Additionally, for each sample the test was repeated targeting areas of different packing. Figure 1 shows images of the hydrophilic (a) and hydrophobic (b) glass beads during the first wetting phase, just before reaching 100 % RH . Testing on glass beads was completed to confirm the ‘classically’ assumed case where menisci, if able, would form concave structures between curved hydrophilic surfaces but convex structures between the same surfaces, at similar separation distances (here, a paradigm of density), when hydrophobic. For brevity, only results from the hydrophobic sand of close packing will be presented here.

3 Preliminary Results

Figure 2 shows a representative selection of the ESEM images, focusing on the evolution of the shape of a liquid bridge forming between two hydrophobic sand particles representative of the larger collection of particles

Figure 2: Evolution of meniscus shape in a hydrophobic sand specimen. [Note that the values under each image indicate the P_{H_2O} and RH respectively]

comprising the specimen. In the beginning of the test there is very little condensation on the particles. Condensation gradually increases in the form of droplets on the particle surfaces until the first asymmetric concave bridge forms (see white arrow in Figure 2c). As the *RH* increases the droplets on the particles coalesce forming a smooth coating of water on the hydrophobic particles. Visual inspection shows that during the initial wetting phase the meniscus shape is rapidly evolving; it grows in volume, expands along the contact line and the contact angle increases ranging from approximately 60° (Figure 2c) to 120° (Figure 2g). Such a result may be considered to agree with the findings of [18], who showed that a liquid bridge may change from a concave to a convex shape as its volume increases. However, here, the significant difference in the shape of the sand particles to the hydrophilic glass beads tested in [18], as well as the change in hydrophobicity, should be considered. Testing completed on hydrophilic sand, prepared to the same degree of packing (to be discussed in detail in an upcoming work), showed no evidence of convex menisci. Therefore, the change in the meniscus shape seen here in Figure 2c to g is attributed to both hydrophobicity and the non-spherical nature of the sand particles that prevents liquid bridges such as the ones described by traditional models between spheres (i.e. as shown in Figure 1) from forming.

After the initial wetting phase, when the sample is dried (Figure 2g to j) menisci do not revert to droplet states on the surfaces of the grains. When wetting, the droplets seem to expand only through droplet coalescence yet do not seem to contract afterwards. At this stage, the menisci either remain (albeit slightly receding and reducing in volume), as it is energetically more favourable, or break forming two large droplets in the contact zones (as multiple droplets would require a larger surface energy). Critically, no evidence of convex bridges after this point was found.

During the final wetting stage (Figure 2j to l), no new bridges form between particles. Areas are observed where the particles are fully submerged in water and others where pre-existing bridges retain their shape. It should be mentioned that Figure 2l appears completely black as the sample has almost reached full saturation (water content affects the ESEM image contrast). The fact that Figures 2g and l, obtained at the same *RH*, have a different degree of saturation indicates significant hysteresis. That this is affected by water coming into contact with the underlying substrate, however, cannot be ruled out at this stage.

One phenomenon not evident in the images presented in this paper, due to their static nature, is that the formation of liquid bridges results in particles being attracted to each other. In hydrophobic granular materials the particles are expected to move apart when the menisci are convex, as such a structure would create a positive pressure in the water meniscus. However, the present results do not support this theory, despite the high contact angles. However, due to the nature of this experiment (one layer of particles adhered onto the peltier stage), we were unable to draw strong conclusions with regards to the positive pore water pressure appearing in convex menisci.

4 Conclusions

The main focus of this work is to study the particle scale changes to meniscus structure while performing a number of wetting and drying cycles on hydrophobic sand specimens. The main findings were:

1. Water first appears on the surface of dry hydrophobic particles in the form of droplets; no adsorbed film is evident.
2. The non-coaxial grain surfaces retard droplets from expanding to create a liquid bridge. The droplets seem to expand only through droplet coalescence and cannot seem to contract afterwards.
3. The shapes of the first menisci are concave but grow and become convex as relative humidity increases, as expected for hydrophobic soils.
4. The non-spherical nature of the sand particles prevents traditional (axisymmetric) liquid bridges from forming and all of the capillary bridges appear to be asymmetric.
5. After the sample becomes fully saturated for the first time the water in the pores recedes at a slower rate, indicating a hysteretic effect.
6. Contrary to recent findings, evidence from real-time visual analyses indicates that the convex capillary bridges between the particles seem to slightly attract the particles.

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