Effect of water film thickness on the degree of water repellency for hydrophobized sand grains

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Abstract: Capillary barrier system is a kind of earthen cover system that can be applied as a final capping system for a waste disposal site. The objectives were to find (i) the effect of water content on the water repellency of sand grains and (ii) the effect of specific surface area and water film thickness on initial contact angle (αi) of different particle size fractions. Toyoura sand and Narita sands with three different size fractions were used. Specific surface areas (SSA) of sand were measured by N2-BET and water vapor adsorption. Sand was mixed with oleic acid to make hydrophobized sand (HS). Water content of HS was changed by adding distilled water. The αi of each sample was measured using sessile drop method. Toyoura has low SSA compare to Narita sands. The αi is decreasing with increasing water film thickness. Further studies are needed on sand hydrophobicity using different materials in the same particle size range.

Keywords: Hydrophobized sand, water repellency, specific surface area, contact angle

1 INTRODUCTION

Capillary barrier system (CBS) is a kind of earthen cover system with low cost and low advanced technique that can be applied to a waste disposal site as a final capping system. It is help to prevent the rainfall infiltration into a waste site and reduce the leachate production. Sloped CBS are help to divert the water more efficiently (Ross, 1990; Stormont, 1996) than non sloped CBS and it will improve the performance of the CBS. Recently, Dell' Avanzi et al. (2010) and Subedi et al. (2012) had been discussed the applicability of hydrophobized CBS which enhance the impermeable properties of the CBS.

In the natural condition, the hydrophobized CBS face to variation in soil-water content over the time due to repeated infiltration and water redistribution processes in soil. They may cause to performance of CBS over the design period. Therefore, it needs to study the changes in degree of water repellency for a hydrophobized coarse layer material with changing water content.

Effects of soil-water content on the degree of water repellency (WR) for different size fractions were studied by de Jonge et al. (1999) using the molarity of ethanol droplets method. The study found single peak and double peak behaviors in WR with changing in soil-water content. Bachmann et al. (2003) assessed wettability of porous material using the Wilhelmy plate method and modified capillary rise method. Those data were compared with the results from the water drop penetration time test and the sessile drop method (SDM). The soil wettability affects to soil-water contact angle (Goebel et al., 2004) which is depend on surface free energy (Roy and McGill, 2002). It is well known that WR changes with water content non-linearly (King, 1981; de Jonge et al, 1999; Goebel et al, 2004, Regalado and Ritter, 2005 and 2009; Kawamoto et al, 2007). Further King (1981) has shown hydrophobicity stable between oven dry and air dry, it was either unchanged or increased between air dry water content and wilting point, and finally decreased rapidly and became wettable near field capacity. Moreover, de Jong et al. (1999) stated that WR increased remarkably from pF 2.5 to 3 for natural hydrophobic sandy soil (pF is the logarithm of the absolute value of matric potential in cm H2O). Karunarathna et al. (2010) found that linear increasing and decreasing of WR with increasing pF. McHale et al. (2005) developed a simple model for a hydrophobic granular surface and that can provide mechanism for enhancement of soil WR through the relative size and spacing of grains and pores.

The development of soil WR is related to hydrophobicity of material (Doerr and Thomas, 2000). Soil particle can be hydrophobized by coating of hydrophobic agents (HA) (Bachmann et al, 2000; Leelamanie and Karube, 2007; Lui et al, 2012). In this study we used oleic acid as a HA and it is a mono unsaturated
omega-9 fatty acid consisting of CH₃ and CH₂ groups, a carboxyl groups (COOH) and a vinyl CH group (double bond CH=CH).

The objectives of this study were to (i) find the effect of water content on the water repellency of sand grains and (ii) the effect of specific surface area and water film thickness on initial contact angle (αi) of different particle size fractions.

2 MATERIALS AND METHOD

2.1 Soil samples preparation

In this study, Toyoura sand (0.25-0.105 mm) and Narita sandy soil, Japan were used. The Narita sandy soil was used after sieving into three different particle size fractions, that were Narita small (0.105-0.25mm), Narita middle (0.25-0.42 mm) and Narita large (0.42-0.84 mm). Figure 1 shows the particle size distribution for each sand fraction. Table 1 show all physical properties and these predetermined bulk densities were used during the repacked sample making for the sessile drop method (SDM) (Bachmann et al, 2000; Buczko and Bens. 2006; Lamparter et al, 2010; Liu et al, 2012).

Sand grains were coated by a “mixing method” (Subedi et al, 2012) with oleic acid (OA) (molar mass of 282.46 g/mol, density of 0.895 g/cm³; Kanto chemical corporation, Tokyo) with different amount of 1, 3, 5, 7, 10 and 15 g/kg for Narita sand and 1, 5, 6 and 10 g/kg for Toyoura sand. Prior to the OA coating, sand was washed with a low-foaming neutral cleansing agent, and then rinsed thoroughly with distilled water for several times. Washed sand was air dried and stored in a climate control room (20°C, 10 and 15 g/kg for Narita sand and 1, 5, 6 and 10 g/kg for Toyoura sand. Prior to the OA coating, sand was washed with a low-foaming neutral cleansing agent, and then rinsed thoroughly with distilled water for several times. Washed sand was air dried and stored in a climate control room (20°C, 0.0 to 0.04 cm3/kg) for two weeks before making hydrophobized sand (HS). After making HS, they were packed in the sealed plastic bag and stored in the climate control room (20°C and 50 % RH) for two days. Water content of the air dried HS were adjusted by adding small amount of distilled water (θ = 0.0 to 0.04 cm3/kg) by 0.005 cm³/cm³ increments. WR of each sand sample was characterized by measuring the initial soil-water contact angle (αi) using the SDM (Bachmann et al, 2000). In the SDM, repacked samples were used and microphotograph of contact angle between water droplet and grain surface was recorded by digital microscope camera system with 100x magnification (VHX-1000, KEYENCE, Osaka, Japan). Figure 2 shows the examples of recorded microphotograph of SDM.

2.2 Soil specific surface area-SSA

(i) SSA by N₂-BET method (SSAN₂)

Specific surface area of sand grains was measured using N₂-BET (SSAN₂) method. For, N₂-BET, a surface area and porosity analyzers (TriStar II Series, Micromeritics instrument corporation, USA) was used. N₂ gas was used as the adsorbent. Triplicate of each washed and dry sand sample (1-2 g) was used.

(ii) SSA by water vapor adsorption (SSATO)

The TO model (Tuller and Or, 2005) is explained water mainly can exist as thin adsorbed films. A specific surface area (SSATO) can be estimated using Eq. (1) (Iwamatsu and Hori, 1996; Tuller and Or, 2005). In Eq. (1), SSA, (m²/kg) was the free fitting parameter.

\[ \theta_m = \rho_w \frac{SSA}{\sqrt{\frac{A_h}{6m - \psi}}} \]  

Where \( \theta_m \) is gravimetric water content (kg/kg), \( \rho_w \) is density of water (kg/m³), \( A_h \) is Hamaker constant (J), g is acceleration due to gravity (ms⁻²), \( \psi \) is the matric head (m H₂O). Adsorbed water film thickness (h in m) can be calculated using Eq. (2).

\[ h = \frac{\theta_m}{\rho_w \frac{SSA}{\sqrt{A_h}}} \]  

20 g of air dry and non coated sand was prepared by adding distilled water (0.02-0.26 g of water by 0.02 increments for 20 g of sand). The samples were mixed well and stored in a sealed plastic bag. Then, the samples were kept for 2 days at 20 °C to allow equilibrium. After 2 days, we conducted water potential measurement with the WP4-T dewpoint potentiometer (Decagon Devices Inc., WA, USA). Immediately
after the measurements we determined the gravimetric water content ($\theta_m$) of each sample by keeping sub sample in an oven at 105° for 24 hours.

![Particle size distribution](image)

**Figure 2** Particle size distribution of Toyoura sand (0.105-0.25 mm) and Narita sand (0.105-0.84 mm)

<table>
<thead>
<tr>
<th>Sand</th>
<th>$\rho_s$ (g/cm$^3$)</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>$D_{50}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toyoura (0.105-0.25 mm)</td>
<td>2.64</td>
<td>1.58</td>
<td>0.17</td>
</tr>
<tr>
<td>Narita small (0.105-0.25 mm)</td>
<td>2.71</td>
<td>1.62</td>
<td>0.19</td>
</tr>
<tr>
<td>Narita middle (0.25-0.42 mm)</td>
<td>2.64</td>
<td>1.58</td>
<td>0.35</td>
</tr>
<tr>
<td>Narita large (0.42-0.84 mm)</td>
<td>2.60</td>
<td>1.56</td>
<td>0.65</td>
</tr>
</tbody>
</table>

![Microscope photograph](image)

**Figure 3** Microscope photograph of water drop on sand grain surface

### 3 RESULTS AND DISCUSSION

#### 3.1 Specific surface area

Figure 3 shows measured values of soil-water potential by WP4-T dewpoint potentiometer and they were fitted with using Eq. 1 (Tuller and Or, 2005; Resurreccion et al, 2011; Arthur et al, 2012). Selected data range for fitting is 4.0<pF<5.5 for all the sand samples. The driest and most wetted data points were not used for SSA calculation and all those data points were omitted. The fitted line is checked with three
Hamaker constant ($A_{sp}$) values which were used by Resurreccion et al. (2011) as of $-1 \times 10^{-20}$, $-6 \times 10^{-20}$, $-10 \times 10^{-20}$ J. The $-6 \times 10^{-20}$ J was well fitted with used sand samples.

Table 2 shows the SSA of each sand fraction by SSA$_{N2}$ and SSA$_{TO}$. All SSA$_{TO}$ of sands are greater than SSA$_{N2}$. Toyoura has low SSA in both methods, as of SSA$_{N2}$ and SSA$_{TO}$ are 1.73 m$^2$/g and 2.7 m$^2$/g respectively. The total SSA of Toyoura is 4 m$^2$/g by the ethylene glycol monoethyl ether (EGME) method (Hamamoto et al., 2008) The HA coated area in sand grains were calculated by dividing the HA amount from SSA (SSA$_{N2}$ and SSA$_{TO}$). Figure 4 shows the HA amount vs. coated area in each sand samples. HA coated area of Toyoura is greater than Narita sand.

![Figure 4 Measured values of soil-water potential were fitted with TO model and specific surface area of grains used as free fitting parameter.](image)

<table>
<thead>
<tr>
<th>Sand</th>
<th>SSA$_{N2}$ (m$^2$/g)</th>
<th>SSA$_{TO}$</th>
<th>SSA$_{EGME}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narita small</td>
<td>10.99 (0.347)*</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td>Narita middle</td>
<td>8.81 (0.558)*</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>Narita large</td>
<td>7.67 (0.408)*</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Toyoura</td>
<td>1.73 (0.155)*</td>
<td>2.7</td>
<td>4**</td>
</tr>
</tbody>
</table>

*Standard deviation of three replicates, ** SSA measured by EGME method (Hamamoto et al., 2008)
Figure 5 shows the $\alpha_i (^\circ)$ changes with increasing OA content (from 0-15 g/kg) of air dry sand of Toyoura and Narita small. The particle size range for both Narita small and Toyoura is between 0.105-0.25 mm (Figure 1). But, WR of these two sands is behaving differently. Toyoura and Narita small produced $\alpha_i > 90^\circ$ at 0.25 g/kg and 1 g/kg respectively (Fig 5), It could be the reason of particle roughness of each fraction (McHale et al, 2005). SSA$_{TO}$ of Toyoura and Narita small is 2.7 and 11 m$^2$/g respectively. It is needed future studies to estimate SSA of this material using any other precise measurement. Plot of the measured $\alpha_i (^\circ)$ with $\theta_m$ and h ($x 10^9$ m) are shown in Figure 6 (data for 1 g/kg OA are shown and others are not shown in this paper). The h ($x 10^9$ m) of HS was calculated respective $\theta_m$ dividing by estimated SSA$_{TO}$ (Eq. 2). Toyoura has drastically reduction of $\alpha_i$ compare to the Narita sand. $\alpha_i$ is become zero for all samples when $\theta_m$ greater than 0.02 kg/kg (Figure 6a). All the Narita sand becomes wettable when water film thickness greater than $\sim 2 x 10^9$ m (Figure 6b). Toyoura sand is become wettable at thickness of 7 x $10^9$ m.
4 CONCLUSION

Initial contact angle of hydrophobized sand is high in air dry sample than water adjusted sample. All the hydrophobized sand samples become wettable at $\theta_m$ of ~ 0.02 kg/kg. Toyoura sand was WR even at ~6 nm of water film thickness and Narita sand became wettable at this water content. At higher water content water molecules can exist as thin film of water or clusters. Further studies are needed with materials which are having similar particle size range.

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6 REFERENCES


