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Application of capillary barriers in wet regions can be problematic due to loss of water-impermeable properties under high-frequency precipitation. In this study, water drop contact angles were examined for sands treated with hydrophobic agents. Results revealed a good potential for using water repellency techniques in capillary barrier systems.

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Characterizing Time-Dependent Contact Angles for Sands Hydrophobized with Oleic and Stearic Acids

Capillary barriers (CBs) represent useful, low-cost systems for limiting water infiltration and controlling seepage at solid waste landfills in semiarid and arid regions. The application of CBs in wet regions can be problematic due to loss of water-impermeable properties under high-frequency precipitation. A potential solution is to alter soil grain surfaces to become water repellent by mixing or coating the soil cover material with hydrophobic agents (HAs). In this study, hydrophobic CBs comprised of sands mixed with environmentally friendly HAs (oleic acid [OA] and stearic acid [SA]) were studied. Water repellency (WR) characteristics for hydrophobized sand samples with different HA contents and representing different coating methods (mixing in and solvent aided) were measured. Initial contact angles (α_i) for OA-coated samples sharply increased with increasing HA content and reached peak values of 97 to 101° at 0.75 to 1.0 g HA kg^{-1} sand, whereafter $\alpha_{\rm i}$ gradually decreased. Measured α_i values for SA-coated samples increased sharply to 90° and then gradually reached a maximum of 108° at 6.0 g kg⁻¹ HA content. Each test sample exhibited a decrease in contact angle (α) with time (t) and reached an apparent equilibrium after around 1200 s. The time dependence of α was expressed by an exponential function, $\alpha = \alpha_i \exp(-At)$, where A is the coefficient of temporal change in WR (s⁻¹). While the A values for the solvent-aided OA-coated samples were relatively constant (between 3 imes 10⁻⁴ and 6 imes 10⁻⁴ s⁻¹), A values for the mixing-in OA-coated samples fluctuated. Generally, the solvent-aided coating method yielded less time dependency of α and higher WR persistence.

Abbreviations: CB, capillary barrier; HA, hydrophobic agent; MED, molarity of ethanol droplet; OA, oleic acid; SA, stearic acid; SDM, sessile drop method; WDPT, water drop penetration time; WR, water repellency.

A capping system is the final component in the construction of engineered sanitary landfills. The proper design of such a system is essential to minimize water percolation into the underlying waste and to control landfill gas emissions. To assure adequate long-term performance, various types of capping systems have been developed to fulfill regulatory standards, including highly technical and expensive systems such as geomembranes and geosynthetic clay liners (Koerner and Daniel, 1997; Simon and Müller, 2004). Although modern engineered capping systems are technically effective, they do not provide a feasible solution for landfills located in developing countries due to economic and technical constraints, as shown in Table 1.

Recently, earthen covers such as CBs and evapotranspirative covers have been proposed as technically feasible and low-cost solutions for limiting water infiltration and controlling seepage at solid waste landfills. The CBs can be constructed in various designs, typically consisting of a fine-grained layer overlying a coarser grained layer (Wing and Gee, 1994; Stormont, 1995). In evapotranspirative covers, there is no increase in storage capacity, rather water uptake by plants and evapotranspiration (ET) prevents deep percolation. The evapotranspirative covers can be used not only as monolithic ET covers, but also as capillary barrier ET covers, and anisotropic barrier ET covers in combination with CBs (Dwyer, 2001; Albright et al., 2003; Scanlon et al., 2005).The earthen cover systems have proved to be effective for landfills located in semiarid and arid regions (Benson and Khire, 1995; Sharma and Reddy, 2004). Their application in wet regions can be problematic, however, because under high-precipitation events, their impermeable properties may be compromised in the long term (Koerner and Daniel, 1997).

One possible technique to enhance the impermeable properties of CBs is to make soil grain surfaces water repellent by mixing or coating the earthen cover material with

Table 1. Requirements for capillary barriers in earthen cover systems summarized from Sharma and Reddy (2004), Simon and Müller (2004), and Benson and Khire (1995).

No.	Item	Key point	Description
1	site specific	use of locally available materials	construction materials are easily available in rural areas
2	low cost	less investment and maintenance cost	use of available construction materials is proved to be cost effective
3	sustainable	durable and long-term performance	design system performs well for controlling infiltration and surface water seepage for desired periods
4	environmentally friendly	use of environmental friendly materials and technologies	construction materials are nontoxic and do not harm human health or the environment
5	engineered	easy construction	proposed system is easy to construct with locally available manpower and skills

HAs. The effectiveness of HA application to enhance the WR for soil grain samples was exemplified in Leelamanie and Karube (2009a,b) and Bachmann and McHale (2009). Leelamanie and Karube (2009a,b) used hydrophobized sands coated with different amounts of SA (in g HA kg⁻¹ sand), evaluated the WR based on the water drop penetration time (WDPT) (Watson and Letey, 1970), and measured contact angles by means of the sessile drop method (SDM) (Bachmann et al., 2000a,b). They demonstrated that both the WDPT and contact angle, α , for SA-coated samples increased with increasing additions of HA to reach a maximum $\boldsymbol{\alpha}$ = 110° at 5 g kg⁻¹ HA. They also reported an exponential decrease in α with time. Bachmann and McHale (2009) measured α for different-textured soil samples coated with different amounts of dichlorodimethylsilane using the SDM and reported α values ranging from wettable ($\alpha = 0^{\circ}$) to $\alpha > 150^{\circ}$. The use of hydrophobized sands to create a CB was tested by Dell'Avanzi et al. (2010), who used sand mixed with polytetrafluorethylene to improve the hydraulic properties and seepage control in the CBs in laboratory experiments. They reported that the hydrophobized sands were effective in controlling lateral drainage, making them a candidate material for final landfill cover systems.

Applying CBs comprised of hydrophobized sands to landfills located in wet regions not only involves examining the WR characteristics and seepage control but also selecting low-cost, environmentally friendly, and locally available materials (see Table 1). In all wet tropical regions, coconut (*Cocos nucifera* L.)is a popular fruit that is used to produce hydrophobic materials such as OA and SA. These acids are plentiful in wet regions and harmless to humans and the environment, and they have the potential as HAs for landfill capping materials. Very little research has been undertaken, however, on the WR characteristics of hydrophobized sands using OA and SA. Particularly, the time dependence of the measured contact angles for the hydrophobized sands is poorly understood quantitatively.

One of the major practical concerns of using hydrophobized sands in field-scale CBs is the natural degradation of hydrophobic agents. Moucawi et al. (1981) measured the decomposition of fatty acids in different soils and reported that decomposition of the organic matter depended on the soil characteristics and the chemical and physical weathering processes. They also reported that the percentage of decomposition for both OA and SA increased with increasing time and reached 31.2 and 41.4%, respectively, after 4 wk in a brunic luvisol soil. The persistence of HAs on hydrophobized sands influences the long-term performance of CBs. As a first necessary step, however, this study focused on the short-term evaluation of WR for hydrophobized sands without considering the effect of HA biodegradation.

The objectives of this study were (i) to assess WR characteristics of sands hydrophobized with HAs such as OA and SA based on the measured contact angles, and (ii) to evaluate the time dependence of the contact angles for the tested hydrophobized sands by a newly introduced exponential function.

Materials and Methods Sample Preparation

Sand from Toyoura, Japan, with a particle size range from 0.105 to 0.21 mm was used as the base material for preparing the mix of sand with HAs. Before the HA coating, the sand was washed with a low-foaming neutral cleansing agent, rinsed with distilled water several times, and air dried. Cleaning helps to remove the dust and boost the adhesion bond between a HA and the sand (Israelachvili, 1991). Oleic acid (molar mass of 282.46 g mol⁻¹; Kanto Chemical Corp., Tokyo) and SA (molar mass of 284.48 g mol⁻¹; Kanto Chemical Corp.) were used as HAs in this study. Oleic acid is a monounsaturated omega-9 fatty acid consisting of CH₃ and CH₂ groups, a carboxyl group (COOH), and a vinyl CH group (double bond CH=CH). Stearic acid is a saturated fatty acid with 18 carbons with no double bonds, consisting of CH₃ and CH₂ groups and a carboxyl group (COOH). Both OA and SA are common organic acids found in various vegetable and animal sources (Gunstone, 2004).

Hydrophobized sand samples with different HA contents (in g HA kg⁻¹ sand) and different coating methods (mixing in or solvent aided) were used for the assessment of WR. The pretreatment procedures for the hydrophobized samples are shown in Fig. 1. For the OA-coated samples, both the mixing-in and solvent-aided methods were used. The sands were either mixed thoroughly with liquid OA in a plastic bag and stored at



Fig. 1. Pretreatment procedures for samples before assessment of water repellency.

constant room temperature (20°C) for 48 h to equilibrate (mixing-in) or immersed in a small container filled with OA-dissolved diethyl ether and kept in a draft vacuum chamber for 3 h to allow volatilization of the diethyl ether. Thereafter, the samples were stored for 48 h at constant room temperature (solvent-aided). For both procedures, 12 different OA concentrations in the coated samples, 0.125, 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 10.0, and 20.0 g kg⁻¹, were prepared. For the SA-coated samples, only the solvent-aided method was used for sample preparation because SA is in powder form at normal room temperature. Ten different SA concentrations in the coated samples, 0.125, 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 g kg⁻¹, were prepared.

After obtaining OA- and SA-coated, hydrophobized sand as described above, the samples were then prepared for the experiments through wetting and drying cycles (Fig. 1). A coated sample was first packed in a cylindrical ring (5 cm in diameter and 1 cm high) at a dry bulk density of 1.58 g cm⁻³ and saturated with distilled water using a hanging water column setup. Water was supplied from the bottom of the packed sample via a glass filter with a positive pressure of 1 cm. While wetting the samples, 1-cm slow water imbibition was maintained for 24 h until the hydrophobized sand was fully saturated. The saturated sample was kept for 12 h and then drained at -30 cm hydraulic head. After cessation of drainage, the sample was removed from the cylindrical ring and stored at a constant room temperature (20°C) for 3 d.

Chemical Characterization

Organic C (OC) contents present in OA-coated samples (for both the mixing-in and the solvent-aided methods) and SA-coated samples (solvent-aided only) were measured by an automatic CN analyzer (CHN corder MT-5, Yanako, Kyoto, Japan). Figure 2 shows the measured OC values compared with calculated OC values based on the mass of C applied through the HA coating. The measured OC values increased linearly with an increase in HA contents but were slightly lower than the calculated values for each sample, indicating a loss of small amounts of added HA during sample preparation, either in the mixing process in the bag or in the volatilization process in the draft vacuum chamber.

Fourier-transform infrared (FT-IR) spectral studies for the OA- and SA-coated samples (HA content $\leq 6 \ \mathrm{g \ kg^{-1}}$) were also performed. The FT-IR spectra were recorded in transmission mode on a spectrometer (Nicolet 6700 FT-IR spectrometer, Thermo Fisher Scientific, Waltham, MA) using samples mixed with spectroscopic-grade KBr. For all spectra, 32 scans were performed at a resolution of 4 cm⁻¹ and an analyzed range from 4000 to 400 cm⁻¹. Measured FT-IR spectra for OA-coated samples (mixing-in) with different HA contents including 0 g kg⁻¹ (bare sand) are shown in Fig. 3a. The FT-IR spectra were analyzed for two adsorption bands that indicate the hydrophobic (CH–) and hydrophilic (CO–) functional groups: Band A represents combined bands from 2800 to 3020 cm⁻¹ including hydrophobic CH₂ (2850 cm⁻¹) and CH₃ (2925 cm⁻¹)



Fig. 2. Comparison between measured and calculated organic C (OC) content for (a) oleic acid (mixing-in), (b) oleic acid (solvent-aided) and (c) stearic acid (solvent-aided) samples. Error bars show standard deviations of triplicate measurements.



Fig. 3. Fourier-transform infrared spectrum for (a) oleic acid (mixing-in) samples and (b) calculated hydrophobic to hydrophilic functional group band (A/B) ratios as a function of hydrophobic agent (HA) content.

vibration modes, while Band B represents combined bands from 1580 to 1800 cm⁻¹ including hydrophilic C=O (1760 cm⁻¹) and OH (1640 cm⁻¹) vibration modes. Ellerbrock et al. (2005) suggested that the A/B ratio (hydrophobic to hydrophilic functional group bands) in the FT-IR spectra could be used to characterize the hydrophobicity of samples and reported a positive relationship between the A/B ratio and measured contact angles for natural forest soils. Calculated A/B ratios as a function of HA content for the OA- and SA-coated samples are depicted in Fig. 3b. With increasing HA contents, the A/B ratios for all samples increased, with some variations. The mixing-in procedure for the OA-coated samples produced a larger increase in A/B ratios than the solvent-aided procedures for both OA and SA samples, especially in the range of HA ≥ 1.0 g kg⁻¹.

Water Repellency Tests

The degree of WR of the samples was assessed with the WDPT test, the molarity of ethanol droplet (MED) test, and the SDM. In the WDPT test, a small drop of distilled water (50 \pm 5 μ L) was placed on the surface of a sample packed in a cylindrical ring at a dry bulk density of 1.58 g cm⁻³ (corresponding total porosity of 0.4 cm³ cm⁻³) using a microsyringe, and the time taken for the water droplet to infiltrate the samples was recorded starting immediately after the water droplet was observed above the sand surface (Watson and Letey, 1970). For each sample, triplicate measurements were made. A maximum recording time for WDPT was set to be 3600 s in this study.

The MED test was used to determine an apparent initial contact angle, $\alpha_{\rm i}$ (°), for the samples (King, 1981; Roy and McGill, 2002) by applying pure water and ethanol solutions of 0.01 to 0.50 kg kg⁻¹ in 0.01 kg kg⁻¹ steps in a constant-temperature room at 20°C. Similar to the WDPT test, a sample packed in a cylindrical ring at a dry bulk density of 1.58 g cm⁻³ was used for the MED test. The test measures the liquid surface tension of an aqueous ethanol droplet (50 \pm 5 μ L) on the sample surface that can infiltrate the sample in 10 s, γ (N m⁻¹), and then the measured γ was related to the temporal change in the surface free energy of solids, $\gamma_{\rm s}$ (N m⁻¹) (Carrillo et al., 1999):

$$\gamma_s = \frac{\gamma}{4\Phi^2} \tag{1}$$

where Φ is the interaction parameter, which is a function of the molecular properties of the solid and liquid and has an empirical value ranging from 0.5 to 1.15 (Adamson and Gast, 1997).

The γ_s (solid–vapor surface tension) was calculated using the equation developed by Carrillo et al. (1999) by combining the equations of Good and Girifalco (1960) and Young (1805):

$$\cos\alpha = 2\Phi \left(\frac{\gamma_s}{\gamma_L}\right)^{1/2} - 1$$
[2]

where γ_L is the liquid-vapor surface tension (water) (N m⁻¹).

Carrillo et al. (1999) substituted Eq. [1] into Eq. [2], so the measured γ value was converted to $\alpha_{\rm j}$:

$$\cos \alpha_{i} = \left(\frac{\gamma}{\gamma_{L}}\right)^{1/2} - 1$$
[3]

In the SDM, a sessile drop contact angle was measured as a function of time *t*, $\alpha(t)$ (°), as proposed by Bachmann et al. (2000a,b). Sample grains with a mass of around of 0.1 g were sprinkled uniformly onto about a 6-cm² adhesive tape, which was fixed on a glass slide. The glass slide was then tapped carefully to remove excess grains. After placing a small drop of distilled water on the grain surface, microphotographs of the contact angle between the water droplet and the grain surface were recorded with a digital microscopic camera system with 100× magnification





(VHX-1000, KEYENCE Corp., Osaka, Japan). Figure 4 shows examples of recorded microphotographs for contact angles of 100 and 60°.

For both contact angles [α_i from the MED test and $\alpha(t)$ from the SDM], higher values for the contact angles represent higher WR of the tested samples. We also note that the measurable α_i range from the MED test is 90° < α_i < 109° (Carrillo et al., 1999), while the SDM can generally evaluate contact angles with $\alpha(t) > 10^\circ$ (Leelamanie et al., 2008).

Results and Discussion Initial Contact Angles for Hydrophobized Sands

The values of α_i measured by the MED test and α (t = 0 s) by the SDM (which is equivalent to α_i), as a function of HA content, are shown in Fig. 5, as are the measured WDPT values. The α_i values measured by the MED test were in good agreement with those measured by the SDM in the range of $\alpha_i > 90^\circ$ for each sample.

For the OA-coated samples (mixing-in, Fig. 5a, and solvent aided, Fig. 5b), the measured α_i values increased sharply with increasing



Fig. 5. Initial contact angles, α_i , measured as a function of hydrophobic agent (HA) content by the molarity of ethanol droplet (MED) test and the sessile drop method (SDM) for (a) oleic acid (mixing-in), (b) oleic acid (solvent-aided), and (c) stearic acid (solvent-aided) samples. Results from the water drop penetration time (WDPT) test are also shown. Note that the *x* axis used in (c) is different from those in (a) and (b).

HA content and reached peak values of 101° at 1.0 g kg⁻¹ (mixing in) and 97° at 0.75 g kg⁻¹ (solvent aided). After the peak values, α_i gradually decreased with increasing HA content. Correspondingly, the WDPT values were highest at the peak values of α_i : at 250 s for $\alpha_i = 101^{\circ}$ (mixing in) and 52 s for $\alpha_i = 97^{\circ}$ (solvent aided).

For the SA-coated samples (solvent aided in Fig. 5c), the measured α_i values increased sharply to around 90° and then gradually reached a maximum of 108° at 6.0 g kg⁻¹ HA. The measured WDPT values corresponding to $\alpha_i > 103^\circ$ for the SA-coated samples exceeded 3600 s. Similar results for α_i were obtained for SA hydrophobized sands by Leelamanie and Karube (2009a,b). They observed that the α_i values exceeded 90° at 1.0 g kg⁻¹ HA (corresponding WDPT > 3600 s) and increased gradually up to $\alpha_i = 110^\circ$ at 5.0 g kg⁻¹, where sand particles were considered to be fully coated with SA. Similar results were also reported by Fink (1970), who measured contact angles for hydrophobized sands with various commercially available organic coating materials using a breakthrough (water imbibition) pressure technique and showed that the contact angles reached relatively constant values of 150 to 160° after a sudden increase in contact angles with larger additions of coating materials.

As already shown in Fig. 3b, the A/B ratio for each treated sample increased with increasing added HA content, indicating that the grain surface tends to become more hydrophobic with increasing HA content. For OA-coated samples (Fig. 5a and 5b), however, the measured α_i decreased after peaking at around 1.0 g kg⁻¹ and did not correspond to the hydrophobic trend based on the A/B ratio. We cannot fully understand this discrepancy, but a high amount of added OA might reduce the contact angle at the grain–water surface due to the multilayer coverage of the grain surface in which a hydrophilic end may be facing outside due to the excess OA.

The results for samples exposed to wetting and drying are shown in Fig. 6 and can be compared with the SDM results for normally prepared HA-coated samples (Fig. 5). For OA-coated samples (mixing in, Fig. 6a), there was no significant difference in measured α_i values ($\Delta \alpha_i$) in the HA content range ≤ 3.0 g kg⁻¹ including the peak values ($\Delta \alpha_i < 0.5^\circ$). In the HA content range >3.0 g kg⁻¹, however, the α_i values for the samples after the wetting and drying cycle became a little lower than those from the normally prepared samples with the maximum $\Delta \alpha_i = 8^\circ$. For SA-coated samples (solvent aided, Fig. 6b), the $\Delta \alpha_i$ values for the samples were low throughout the whole range of HA content and ranged from 0.8 to 2°.

Similar results have been reported in previous studies for natural soils. The WR is known to diminish with time when the material is wetted and is reestablished as the soil dries (Dekker and Ritsema, 1994; Doerr and Thomas, 2000; Lamparter et al., 2009; Bachmann et al., 2007). Doerr and Thomas (2000) suggested that the restoration of hydrophobicity after a wetting and drying cycle was not only caused by soil moisture loss but also by rearrangement of the organic molecules, as also pointed out by Ma'shum and Farmer (1985).



Fig. 6. Effect of increasing hydrophobic agent (HA) on the initial contact angle, α_i , in hydrophobized Toyoura sand before and after the wetting and drying cycle for (a) oleic acid (mixing-in) and (b) stearic acid (solvent-aided) samples.

Time Dependence of Contact Angles for Hydrophobized Sands

The observed time dependence of the contact angles, $\alpha(t)$, measured with the SDM is plotted in Fig. 7 for selected samples. Corresponding to the observed $\alpha(t)$ values, the temporal change in the surface free energy of the solids, γ_s (N m⁻¹), is also shown in the figure.

In Eq. [2], the value of Φ was set as 0.6 (Gilboa et al., 2006) and the γ_L of water as 0.728 N m^{-1} at 20°C.

Each test sample exhibited a gradual decrease in $\alpha(t)$ and a gradual increase in $\gamma_s(t)$, and reached an apparent equilibrium after 1200 and 1800 s of the solid (grain)–water contact time for OA-coated samples (mixing in and solvent aided) and SA-coated samples (solvent aided).

The reduction in the contact angle (i.e., WR) with contact time can be mainly explained by adsorption of water molecules onto the grain–water contact surface and the consequent increase in the surface free energy (Leelamanie and Karube, 2009a; Bachmann et al., 2007). Likewise, the time dependence of the contact angle has been partially attributed to the grain–water surface interactions that lead to a reduction in the liquid surface tension (Goebel et al., 2004). In addition, the change in orientation of hydrophobic–hydrophilic functional groups with contact time might have reduced the WR for the tested samples (Doerr and Thomas, 2000; Ellerbrock et al., 2005).

In this study, the temporal change in $\alpha(t)$ was expressed by a simple exponential function:

$$\alpha = \alpha_i \exp(-At)$$
^[4]

where α_i is the initial contact angle (°) $[\alpha(t) = 0 \text{ s}]$ and A is the coefficient of temporal change in the contact angle (i.e., temporal change in WR) (s⁻¹). A higher A value gives a higher decrease in the contact angle with time, representing a greater time dependence of the contact angle (see Fig. 7). By rearranging Eq. [2], the temporal change in γ_s can be expressed as

$$\gamma_{s} = \left(2\Phi\right)^{2} \gamma_{L} \left(1 + \cos\alpha\right)^{2}$$
[5]

Fitting the measured $\alpha(t)$ plots with Eq. [4] using the measured α_i values, the A values were determined. The $\gamma_s(t)$ values were subsequently calculated using Eq. [5] and the obtained A values.

The $\alpha(t)$ and $\gamma_s(t)$ curves captured well the temporal change in the contact angle and the surface free energy of the solids for all measurements (Fig. 7). The fitted A values for all the tested samples are plotted in Fig. 8 as a function of HA content. The A values for the mixing-in OA-coated samples fluctuated widely within the range from 4×10^{-4} to 22×10^{-4} s⁻¹ (Fig. 8a). The large fluctuation can be observed in the pretreated samples after the wetting and drying cycle. For the mixing-in OA-coated samples, it is interesting to note that minimum A values were recorded at the HA content of 1.0 g kg⁻¹, giving the peak values of α_i (=101°) (Fig. 5a and 6a). On the other hand, the A values for solvent-aided OA- and SA-coated samples were relatively constant, ranging from 3×10^{-4} to 6×10^{-4} s⁻¹.

The results of calculating A values using the previously reported data for SA-coated samples (solvent aided) in Leelamanie and Karube (2009a) are also given in Fig. 8b. The A values reported in the literature (Leelamanie and Karube, 2009a) were a little larger than our data but exhibited only small fluctuations. This suggests that the solvent-aided samples are less time dependent and exhibit higher WR persistence than the mixing-in samples.



Fig. 7. Contact angles, α , and soil surface free energy, γ_s , as a function of soil-water contact time for (a,d) oleic acid (mixing-in), (b,e) oleic acid (solvent-aided), and (c,f) stearic acid (solvent-aided) samples.



Fig. 8. Effect of increasing hydrophobic agent (HA) on the time-dependence index, *A*, in hydrophobized Toyoura sand before and after the wetting and drying cycle for (a) oleic acid (mixing-in) and oleic acid (solvent-aided) samples and (b) stearic acid (solvent-aided) samples. Note the different *y* axes.

Figure 9 illustrates the time-dependent characteristics for the contact angle expressed by the newly introduced functions (Eq. [4] and [5]). Half of time *t*, $t_{1/2}$, corresponding to half the value of the initial contact angle, $\alpha_i/2$, can be simply expressed as $t_{1/2} = \ln(2)/A$ (Fig. 9a). Correspondingly, the surface free energy of the solids at $t_{1/2}$, $\gamma_s(t_{1/2})$, can be expressed as $\gamma_s(t_{1/2}) = (2\Phi)^2 \gamma_L [1 + \cos(\alpha_i/2)]^2$ (Fig. 9b). Figure 9c illustrates the sensitivity of the *A* values to the time dependence of the contact angle. Higher *A*

values give a higher temporal change in the contact angles (i.e., greater time dependence). For example, if the *A* value doubles ($A_2 = 2A$ in Fig. 9c), the half time corresponding to $\alpha_i/2$ becomes half the value, as $\ln(2)/2A$.

In this study we examined the WR characteristics of sands hydrophobized with HAs such as OA and SA based on the measured contact angles. In perspective, for characterizing the coating of



Fig. 9. Time-dependent characteristics of the contact angle expressed by an exponential function, $\alpha = \alpha_i \exp(-At)$ where *A* is a time-dependence index, α_i is the initial contact angle, and *t* is time, for (a) determination of the half time, $t_{1/2}$, corresponding to $\alpha = \alpha_i/2$, (b) determination of the soil surface free energy $\gamma_s(t_{1/2})$ at $t_{1/2}$, and (c) sensitivity of *A* values to $t_{1/2}$. Note that the higher the *A* value, the higher the time dependence of α .

HAs on the sand grains, the coating mechanism should be further analyzed and discussed. The persistence of HAs on hydrophobized sands depends on the biodegradation of organic matter by microbial activities (Franco et al., 2000; Wallis and Horne, 1992), suggesting that the effect of microorganisms on the biodegradation of HAs should be further examined. Regarding the application of hydrophobized sands to the CBs in landfill capping systems, their ability to control seepage should be investigated through their hydraulic properties such as water retention curves and unsaturated hydraulic conductivities. Regarding the field-scale practical applicability of the proposed sand treatment procedure, further investigation and analysis should be performed in terms of its feasibility and sustainability. In addition, countermeasures to overcome prolonged flooding due to intense heavy rainfall on hydrophobized CBs should be further analyzed by investigating the effects of surface water flow and flood control mechanisms.

Conclusions

The WR of hydrophobized sand samples with different OA and SA contents was quantified using MED, SDM, and WDPT methods. Adding small amounts of hydrophobic OA and SA in soil can induce WR. For solvent-aided and mixing-in OA samples, α_i sharply increased with increasing HA content to reach peak values of 97 to 101° at 0.75 to 1.00 g kg⁻¹ HA and gradually decreased thereafter. For SA-coated samples, the measured α_i values increased sharply to 90° and then gradually reached a maximum of 108° at 6 g kg⁻¹ HA content. Each test sample exhibited an exponential decrease in the contact angle with increasing soil water contact time and reached an apparent equilibrium depending on HA contents. A new exponential function was introduced to capture the time dependence of the contact angle. The parameter A in the exponential function represents the temporal change in contact angle and would be a useful index to characterize the

time dependence of the contact angle. Overall, the sands hydrophobized by OA and SA revealed good performance evaluated by the measured contact angle, implying a good potential for using this technique in CB systems.

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