On the resistance of hydrophobic soil polymer coatings created by cold plasma polymerization

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Abstract. Hydrophobic soils have natural or artificial origin. In this context, some techniques exist to turn into hydrophobic sand that was originally hydrophilic, as most soils in fact are. Its classical application is impermeabilizing structures where water percolation is not desired. In this paper, a new technique to achieve hydrophobicity is described. It consists of coating particles via cold plasma. The process is known to the industry, but its application in geotechnics is not yet described in literature. The monomers used were octafluorcyclobutane (C_4F_8) and 1H,1H,2H,2H-perfluoroctylacrilate (PFA-C6). For each monomer, the material was in the coating chamber during two different time spans and a sample was pretreated with oxygen. Different mechanical, thermal and hydraulic conditions were imposed to the samples in order to evaluate the resistance of the coating and its properties. The hydrophobicity was evaluated by means of Water Drop Penetration Time. Results indicate that longer time spans in the cold plasma chamber lead to a more hydrophobic material and that oxygen pretreatment on the sample is irrelevant. It was also observed that mechanical, hydraulic and thermal procedures influence the coating. These observations lead to optimization of the production process and to the understanding of how the material can be applied in the construction industry and what mechanical/hydraulic loads it can be subjected to.

1 Introduction

Usually, the hydrophobicity of soils stems from a coating, that can be acquired naturally or intentionally. The naturally occurring coating substances, usually of organic origin, can originate from sewage contamination, plants, decaying organic matter, micro-organisms, soil fauna, exposure to high temperatures through fire etc. This achieved hydrophobicity usually is reverted after prolongated contact with water. Its consequences are a higher water runoff and more easily erodible soil. Groundwater pollution is also facilitated by the property, as a result of preferential flow [1].

Regarding artificial coatings, those can be intentionally applied, aiming at a specific applicability of that soil. Between those, the construction of a water restraining layer is the most common use, for example in a pavement system or in a dam core [2]. Those possible applications legitimate the ongoing research on this kind of material.

The usual and in literature most described way to intentionally coat soil particles is by mixing it with dimethyl-trichlorosilane (DMS), polydimethylsiloxane (PDMS) or dichlorodimethylsilane (DMSCS) [2]. In this paper a new technique to coat the particles is described and employed, namely cold plasma polymerization. This application of it is not yet described in literature. Fig. ***1*** presents an example of a hydrophobic material, on the surface of which a water drop is resting. For an uncoated sample, the water drop would penetrate instantaneously and it would not be possible to take a picture.

Fig. 1. Drop of dyed water resting on the surface of a hydrophobic sand sample.

Contact angle is the microscopic property that governs wettability [3], indicated by θ in Fig. ***2***. This property describes the hydrophobicity magnitude. It is the angle between the solid surface and the intersection of both fluids, given mechanical equilibrium, and evolver around the triple-line, the geometric intersection of air, liquid and solid phases.

A completely hydrophobic material would have an infinite drop penetration time. The fact that the drop penetrates after a time interval indicates that the soil water repellency can decrease as the material is wet. As contact angle describes the hydrophobicity magnitude, the WDPT describes its persistence [4].

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Given this context, this study consists in testing the hydrophobicity of cold plasma coated materials after exposing it to different laboratory and simulated field conditions. The results indicate if and how the coated material can be used in the field, and also point towards possible improvements in the technique.

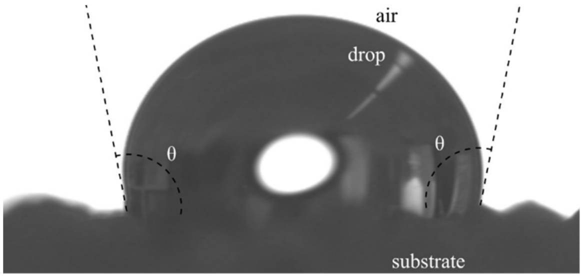

Fig. 2. Contact angle measurement with the Sessile Drop Method.

2 Methodology

2.1 Hydrophobic coating of the sand

In this study, eight types of artificially hydrophobized materials were used. The base material is Hamburg Sand, a model soil at Hamburg University of Technology, and glass beads with similar granulometry (soda-lime glass—SiLi beads type S, manufactured by Sigmund Lindner GmbH, Germany). Both materials are naturally hydrophilic. The glass beads are employed in order to evaluate the influence of the grain shape in the result, given that they are almost perfectly round, while soil grains have completely random shapes. Table 1 [5] presents the main properties of both substrate materials employed.

In order to make them hydrophobic, a process named cold plasma polymerization was employed. It consists of inserting a monomer and an uncoated material in a chamber and using energy via plasma to convert the substance in a grain coating polymer [6]. Monomers used were octafluorcyclobutane (C4F8) and 1H,1H,2H,2H-perfluoroctylacrilate (PFA-C6). The technique has already been used to coat hydrogels [7], clothing fabrics [8] and although it is known to the industry, there is so far no description in literature of its employment for hydrophobizing soil. The uncoated and thus hydrophilic versions were also tested in this study, in order to enable comparisons. The differences between the eight hydrophobic materials are described in Table 2.

2.2 Hydrophobicity testing

Laboratory tests that do not require extensive equipment can be performed to determine the hydrophobicity degree of a sample. Mainly, three tests are used in order to measure hydrophobicity and categorize samples according to it: SDM (Sessile Drop Method), WPDT (Water Drop Penetration Time) and EP (Ethanol Percentage) test. The test used in this study was the WDPT.

While SDM is about in measuring directly the contact angle exactly after the drop is placed (Fig. ***2***), the WDPT test consists of placing a water drop with a specific volume on the surface of the material and measuring how long it needs to completely penetrate the substrate.

In literature, the WDPT test is not standardized and has been employed with different parameters by different authors. Variables are the number of averaged drops, volume of the drop and categories in which the result is classified. [9] summarizes the already adopted parameters. In this paper, three 50 microliter drops were averaged, according to [10] and [4]. This procedure intends to remove the influence of local heterogeneities. A laboratory pipette (10 - 100 μL model from APEX CE SPECIALIST LIMITED, according to DIN 12650 [11]) was used to produce drops with the exact volume. The environment in which the tests were performed was a geotechnical laboratory with atmospheric temperature.

As the employed test does not measure the contact angle and only qualifies and not quantifies the hydrophobicity of a material, it can be classified as an index test. Even though, in [4] the standard deviation of the measures obtained for this test was up to 600 s.

Regarding the hydrophobicity degree classification according to the WDPT test results, there is more than one criterion available. [9] presents a summary of values adopted by other authors, which are presented in Table 3. In this study, the criterion used will be the one presented in columns one and two of Table 4 and developed by [10], which is similar to the one used by Bisdom *et al.* (1993) apud [9] in Table 3.

2.3 Hydrophobicity resistance to laboratory and simulated field conditions

Samples were exposed to some usual field and laboratory conditions in order to evaluate the resistance of the coating to it. Hydraulic and mechanical procedures were imposed. In order to observe the resistance against mechanical abrasion, samples of each material were sieved. Samples were also put in the muffle furnace to evaluate the ignition of the organic coating. Lastly, the influence of water on the samples was measured by exposing the samples to different saturation degrees and washing them under running water.

3 Results and discussion

The first step of data processing was removing the samples with WDPT in the original state smaller than 60 seconds, which are classified as slightly water repellent by [10]. As a result, samples V1 and V3, respectively Hamburg Sand coated with C4F8 treated for the shorter time (20 minutes) with and without Oxygen pretreatment, were removed.

Although each sample is tested with three drops at the same time, only the mean value is presented in the following comparisons. Also, the y-axis of the WDPT graphs are limited at 10800, the maximum value from the hydrophobicity classification used by [10].

Table 1. Base Materials main properties [5].

Base material	ρ_s [g/cm^3]	e_{min} [-]	e_{max} [-]	d_{10} [mm]	d_{50} [mm]	d_{max} [mm]
Hamburg Sand	2.64	0.520	0.805	0.45	0.68	2.00
Glass beads	2.50	0.555	0.679	0.45	0.68	1.30

ρ_s: grain density,
e_{min}: min. void ratio,
e_{max}: max. void ratio,
d_{10}: grain diameter at 10% passing,
d_{50}: grain diameter at 50% passing,
d_{max}: max. grain diameter.

Table 2. Eight types of hydrophobic material used in this paper.

Sample Name	Coating Substance - Monomer	Time (minutes)	Pre-treatment	Substrate
V1	C4F8 (octafluorcyclobutane)	20	-	Hamburg Sand
V2		60	-	
V3		20	Oxygen (20 min)	
V4		20	-	Glass beads with similar grain size distribution: Hamburg Glass
V5	PFA-C6 (1H,1H,2H,2H-perfluorooctylacrilate)	20	-	
V6		20	-	Hamburg Sand
V7		60	-	
V8		20	Oxygen (20 min)	

Table 3. Hydrophobicity degrees according to different authors [9].

Classification	WDPT (seconds)					
	Adams et al. (1969)	**Bisdom et al. (1993)**	**Doerr et al. (1996)**	**Ma´shum & Farmer (1985)**	**McGuide & Posner (1981)**	**Roberts & Carbon (1971)**
Hydrophilic	<10	<5	<60	<1	<60	<1
Slightly hydrophobic	10-60	5-60	-	-	-	1-10
Strongly hydrophobic	-	60-600	-	-	-	10-60
Severely hydrophobic	>60	600-3600	-	-	-	>60
Extremely hydrophobic	-	>3600	>3600	-	-	-

Table 4. Hydrophobicity degrees according to [10] (classification used in this study)

Classification	WDPT (seconds)	Classification of samples coated in this study (initial condition)
Hydrophilic/ wettable	<5	V1
Slightly hydrophobic/ water repellent	5-60	V3
Strongly hydrophobic/ water repellent	60-600	-
Severely hydrophobic/ water repellent	600-3600	V2, V4 and V5
Extremely hydrophobic/ water repellent	3600-10800	V6, V7 and V8

3.1 Original results – July and November measurements

The first comparison presented is the WDPT obtained in original unloaded samples, kept the whole time in the container in which they arrived inside at the laboratory. Tests were performed in July and then repeated in November. Fig. *3* presents the obtained values. The last column of Table 4 presents the hydrophobicity degree classification of the samples according to the July results.

It is noticeable that V4 and V5, which have glass beads as substrate, went from strongly (600 - 3600 s) to slightly water repellent (60 - 600 s), loosing almost all its water repellency. For the samples with Hamburg Sand as a substrate, the hydrophobicity increased for both samples whose values were not at the greater limit:

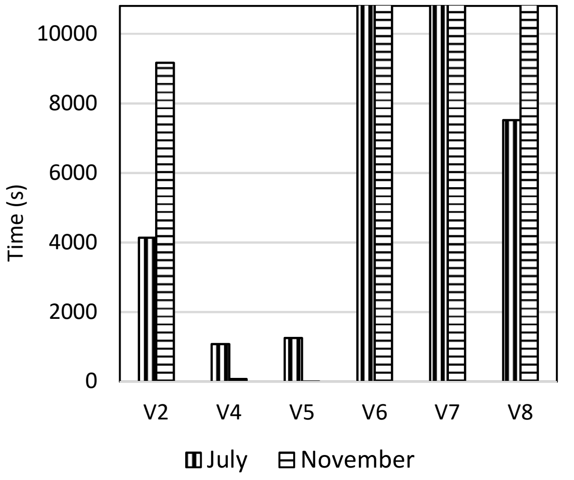

Fig. 3. Comparison between WDPT of original samples obtained in July and November.

V2 and V8. The authors have so far, no explanation for that.

A factor that could influence those results is the season of the year. The first group was performed during Summer and the second during Fall, both in the city of Hamburg. Since the tests were performed in a geotechnical laboratory environment, in which the temperature and humidity are not constant, those two factors probably have greater influence on the subject as expected. In future studies, they must be better controlled.

For the comparisons in the following sections, the WDPT obtained in July were employed, given that the measurement is closer in time to the coating date of the samples.

3.2 Samples placed in the muffle furnace

Samples were placed in the muffle furnace at 550° C for twelve hours, until constant weight, on a procedure named LOI (Lost on Ignition). This test aims at determining the proportion of organic matter on the soil, given that it ignites at this range of temperature.

All the samples lost their hydrophobicity completely after this procedure, reducing their WDPT to 0 second and thus becoming hydrophilic. This is explained by the fact that the coating is organic and thus lost through ignition.

Although the WDPT became 0 seconds for all samples, the proportional mass loss was the same for coated and non-coated samples, variating only according to the substrate. While coated and non-coated Hamburg Sand samples lost around 0.2 % of their mass, coated and non-coated glass beads lost around 0.02%, around 10 times less. This result is a characteristic of the substrate material, regardless of the coating.

3.3 Sieved samples and grain size distribution

To observe if the standard geotechnical procedure of sieving the sample to obtain grain size distribution would affect the samples, they were all sieved according to DIN EN ISO 17892-4 [12]. The sieves used have openings of 63 mm, 20 mm, 6.3 mm, 2.0 mm, 0.63 mm, 0.2 mm and 0.063 mm. WDPT of the original and sieved samples are presented in Fig. ***4***.

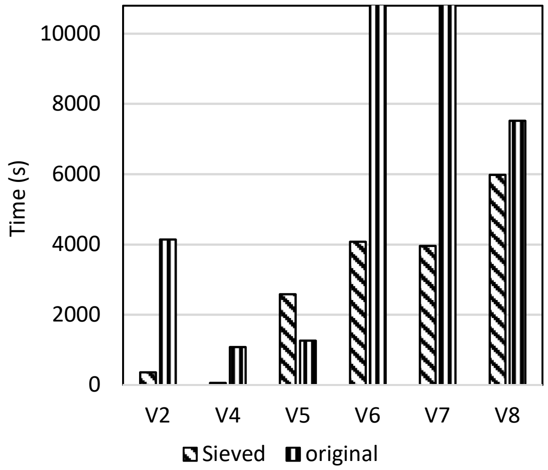

Fig. 4. Comparison between WDPT of original and sieved samples.

While samples V2 and V4, respectively Hamburg Sand and glass beads coated with C4F8 lost almost completely their hydrophobicity, samples V6, V7 and V8, coated with PFA-C6, lost a variable fraction of it. Sample V5 presented a result that the authors do not see an explanation for, increasing its hydrophobicity after being sieved.

The grain size distribution of the coated samples was also compared to the one of the original Hamburg Sand. The obtained curves are presented in Fig. ***5***.

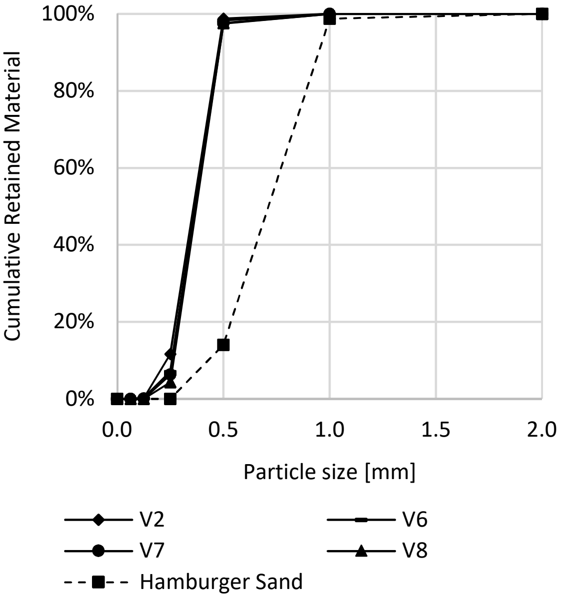

Fig. 5. Grain size distribution of coated and uncoated samples.

It is noticeable that the original Hamburg sand has greater fractions of bigger particles, resulting in greater d_{30} and d_{60}. All the coated sand samples present a similar grain size distribution, with a higher frequency of smaller particles. The authors have no hypothesis to explain that.

3.4 Variable saturation degree

Samples were tested at different saturation degrees. Those were achieved by manually compacting a certain mass of material mixed with a weighted amount of water into a specific volume.

All samples analyzed (V2, V4, V5, V6, V7 and V8) were hydrophilic with more than 10% saturation degree. The WDPT was performed at 10, 20, 40, 60, 80 and 100% and the results were always 0 seconds. After that, tests were also made in all materials with 5% saturation degree, to try to determine if the hydrophobicity still remains at some degree. Samples V6 and V7 were the only ones still severely hydrophobic (3600 s < WDPT < 10800 s) at 5% saturation degree.

3.5 Samples washed under running water for 20 seconds

WDPT measurements of samples washed under running water are presented in Fig. **6**, in which the original WDPT were also plotted to allow comparisons.

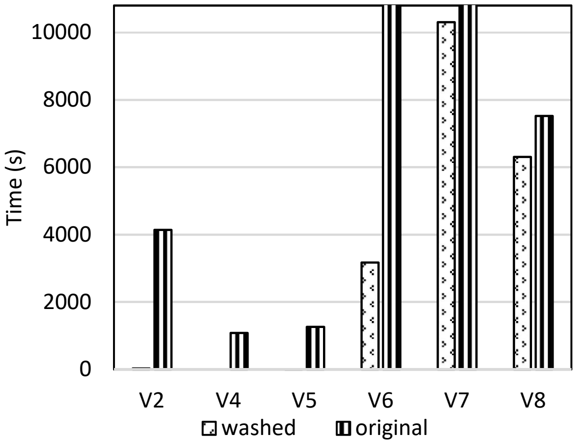

Fig. 6. Comparison between WDPT of original samples and samples washed under running water.

It is possible to conclude that the C4F8 coating (samples V2 and V4) is totally washed away by the water. For samples V4 and V5, coated with different substances but composed of the same substrate, coating was also washed away by water. For samples V6, V7 and V8, all Hamburg Sand coated with PFA-C6 with different parameters, the hydrophobicity was reduced, but not completely removed. Given that the WDPT reduction represents always a different percentage of the original value, other factors are probably also involved in the behavior and influence on the final result.

4 Conclusions

WDPT test was employed to measure the hydrophobicity degree of samples coated with hydrophobic polymers via a cold plasma technique. Samples were exposed to different laboratory and simulated field conditions to evaluate the resistance of this coating to them. Contact angle of those samples was not measured with the SDM technique by the time this paper was published. This is an approach that the authors suggest for future studies.

In summary, exposure to temperatures in the range of 550° C removed completely the coating and thus the hydrophobicity, according to section 3.2.

The results presented in section 3.4 indicate that the hydrophobicity would be completely lost above a saturation degree of 10% and partially lost above a saturation degree of 5%.

Known that samples are frequently and repeatedly exposed to water on real life and field conditions, the coating with C4F8 would be washed and PFA-C6 would have its hydrophobicity reduced according to the results in section 3.5.

Regarding abrasion imposed to the material due to mechanical loadings, results in section 3.3 indicate that it leads to a partial loss of the hydrophobicity. After mechanical abrasion due to sieving, materials coated with C4F8 lost their hydrophobicity almost completely, while materials coated with PFA-C6 lost it partially.

In summary, C4F8 was lost by washing and also by sieving. The PFA-C6 coating was affected, but the sample was still hydrophobic after being washed or sieved, showing that this polymer is the one to be employed in further research on the topic. Other coating substances should also be tested and compared to the presented results in future studies.

Saturation degree above 5% and muffle furnace time converted all samples to hydrophilic. Although temperatures like the one in the muffle furnace are usually not achieved in the field, the saturation degree of field material is usually higher than 5%. This result, then, questions the applicability of the material as it was produced in this study for real-life construction works.

Besides the applied coating, this technology is still expensive and imposes restrictions due to its cost, given that coating 16 kg of sand in Germany costed around 800 Euros in March of 2022.

In addition, in the current cold plasma polymerization process the material is kept still inside the chamber, what could have led to uneven coating of the particles that lead to ineffectiveness. A suggestion for future research on this technique is to move the material inside the chamber during the coating procedure, perhaps by means of a rotating drum.

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References

1. Bardet, J.-P., M. Jesmani, and N. Jabbari, *Permeability and Compressibility of Wax-Coated Sands*, in Géotechnique 64, no. 5; 341–50 (2014) https://doi.org/10.1680/geot.13.P.118.
2. Lourenço, S. D. N., Y. Saulick, S. Zheng, H. Kang, D. Liu, H. Lin, and T. Yao, *Soil Wettability in Ground Engineering: Fundamentals, Methods, and*

Applications, in Acta Geotechnica 13, no. 1: 1–14 (2018) https://doi.org/10.1007/s11440-017-0570-0.

3. AlRatrout, Ahmed, Ali Q Raeini, Branko Bijeljic, and Martin J Blunt, *Automatic Measurement of Contact Angle in Pore-Space Images*, in Advances in Water Resources 109 : 158–69 (2017) https://doi.org/10.1016/j.advwatres.2017.07.018.
4. Lin, Hongjie, and Sérgio D. N. Lourenço. *Physical Degradation of Hydrophobized Sands*, in Powder Technology 367 : 740–50 (2020) https://doi.org/10.1016/j.powtec.2020.04.015.
5. Milatz, Marius, Nicole Hüsener, Edward Andò, Gioacchino Viggiani, and Jürgen Grabe. *Quantitative 3D Imaging of Partially Saturated Granular Materials under Uniaxial Compression*, in Acta Geotechnica 16, no. 11: 3573–3600. (2021) https://doi.org/10.1007/s11440-021-01315-5.
6. Zainal, Muhamad Nor Firdaus, Norizah Redzuan, and Mohd Misnal. *Brief Review: Cold Plasma*, in Jurnal Teknologi 74: 57–61. (2015) https://doi.org/10.11113/jt.v74.4834.
7. Schroeter, Baldur, Isabella Jung, Katharina Bauer, Pavel Gurikov, and Irina Smirnova. *Hydrophobic Modification of Biopolymer Aerogels by Cold Plasma Coating*, in Polymers 13, no. 17: 3000. (2021) https://doi.org/10.3390/polym13173000.
8. Zhang, Gannian, Miguel A. Quetzeri-Santiago, Corinne A. Stone, Lorenzo Botto, and J. Rafael Castrejón-Pita. *Droplet Impact Dynamics on Textiles*, in Soft Matter 14, no. 40: 8182–90 (2018) https://doi.org/10.1039/C8SM01082J.
9. Doerr, Stefan H. *On Standardizing the 'Water Drop Penetration Time' and the 'Molarity of an Ethanol Droplet' Techniques to Classify Soil Hydrophobicity: A Case Study Using Medium Textured Soils*, in Earth Surface Processes and Landforms 23, no. 7: 663–68. (1998) https://doi.org/10.1002/(SICI)1096-9837(199807)23:7<663::AID-ESP909>3.0.CO;2-6.
10. Badía, D., J. A. Aguirre, C. Martí, and M. A. Márquez. *Sieving Effect on the Intensity and Persistence of Water Repellency at Different Soil Depths and Soil Types from NE-Spain*, in CATENA, Soil Water Repellency, 108: 44–49 (2013) https://doi.org/10.1016/j.catena.2012.02.003.
11. "DIN 12650-2 - 1981-10 - Beuth.De." Accessed December 5, 2022. https://www.beuth.de/de/norm/din-12650-2/921477.
12. "DIN EN ISO 17892-4 - 2017-04 - Beuth.De." Accessed December 2, 2022. https://www.beuth.de/de/norm/din-en-iso-17892-4/242947793.