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Influences on the hydrophobicity of concrete surfaces treated with alkyl trialkoxysilanes

Udo Antons
Institute of Building Materials Research, RWTH Aachen University, Aachen, Germany, antons@ibac.rwth-aachen.de

Michael Raupach
Institute of Building Materials Research, RWTH Aachen University, Aachen, Germany, raupach@ibac.rwth-aachen.de

Oliver Weichold
Institute of Building Materials Research, RWTH Aachen University, Aachen, Germany, weichold@ibac.rwth-aachen.de

SUMMARY: This paper focuses on hydrophobic layers in concrete and how alkaline media, UV radiation, and carbonation as well as on-going cement hydration influences the properties of such layers. Single-sided nuclear magnetic resonance measurements show that layers formed by impregnating samples with alkyl trialkoxysilanes are stable even under long-term exposure to alkaline solution and UV radiation, with the damage of the latter being limited to the topmost surface layers. Microstructural changes during accelerated carbonation of blast furnace slag cement based concrete have a major impact on the hydrophobic layer properties, while the carbonation of Portland cement concrete has no influence. On-going hydration additionally influences the hydrophobic layer properties.

KEY-WORDS: durability, failure mechanism, non-destructive testing

INTRODUCTION

The performance of hydrophobic layers formed by the impregnation of concrete can decline due to the exposure to environmental conditions as well as changes in the microstructure upon carbonation and cement hydration. An additional threat to the performance could be the alkalinity of the pore solution, i. e., any fluid phase that builds up inside the pore system of the cement matrix, which can potentially hydrolyse the siloxane (Si–O–Si) links connecting the hydrophobing agent to the surface.

When exposed to UV radiation, the characteristic roll-off behaviour of hydrophobised surfaces vanishes after a certain period of time. Mainly due to this superficial loss of hydrophobicity, water repellent agents have a poor reputation in terms of durability aspects, although several previous investigations indicated that the hydrophobic layer below the affected surface was still intact [1, 2]. This striking difference between perception and actual performance of hydrophobing agents demands a more detailed study of the durability of hydrophobic layers and of the major failure mechanisms in those cases where the ability to prevent the ingress of liquid water has been lost.

However, evaluating the performance of hydrophobic layers after being applied to concrete is not very meaningful. The common method to analyse hydrophobic layers on buildings is to investigate drilled cores, i. e., information on the hydrophobic layer is only gained in very few spots. However, an essential tool for an adequate quality control on site needs to be a simple, fast, and fundamentally a non-destructive test method, which can be applied in a small meshed pattern. Such a method would ultimately allow mapping the state of the hydrophobic layer on a complete building without making it look like Swiss cheese. Additionally, non-destructive testing in the laboratory provides the opportunity to investigate failure mechanisms, i. e., the extent to which an environmental stress affects the performance of hydrophobic layers, without the influence of sample preparation scattering.

A versatile, non-destructive method for the determination of liquids in porous substrates is single-sided nuclear magnetic resonance [3, 4]. Unlike the technology used in chemistry or medicine, in which the samples are inserted into large superconducting magnets, single-sided NMR uses a sender/receiver set-up located at the same side of the sample. Thus, the single-sided method is equally well suited for small lab samples to be analysed as well as the equipment being used on horizontal walls, floors, and ceilings of buildings. However, since the method can only detect liquids and not the dried hydrophobic layer, the evaluation of the hydrophobic layer and the assessment of its performance is indirect. That is, the object under investigation needs to be drenched with water and the hydrophobic layer is then detected by the absence of water at certain depths of the sample. However, the method is not limited to detecting water as the hydrophobization agents can be equally well detected as long as they are still liquid, i. e., during ingress. This allows for single-sided NMR also to be used as a tool in quality control during application.

This paper highlights the application of single-sided NMR to investigate the potential failure mechanisms of hydrophobic layers subject to artificial ageing as exemplified by UV radiation, carbonation, alkaline degradation, and continued cement hydration. It is shown that by analysing changes in the depth profiles recorded by NMR, the failure of hydrophobic layers becomes apparent and the failure mechanisms can be identified. With this knowledge, recommendations on the proper implementation of hydrophobing agents can be made as well as potential faults in the layers of impregnated buildings can be detected.

MATERIALS AND METHODS

Concrete specimens

Plates of 30 x 30 x 5 cm were produced from the mixtures shown in Table 1. Specimens for the investigation of UV radiation, alkaline solution, and carbonation effects were demoulded after one day and subsequently stored under water for 28 days at room temperature. During this storage 30 mm thick and 100 mm wide discs were cut from the plates. The surface, which had been in contact with the mould, was not processed.

Unless noted otherwise, all specimens were conditioned at 23 °C and 50 % relative humidity in an atmosphere containing 2 vol.-% of carbon dioxide until the carbonation front reached a depth of 10 mm before applying the hydrophobing agents. For the evaluation of the carbonation effect, a control set was made and conditioned at 23 °C and 50 % relative humidity for an equal period of time in the absence of carbon dioxide to limit carbonation.

To investigate the effects of cement hydration on the hydrophobic layer, the preparation of the specimens was modified as follows: demoulding after 1 day, subsequent storage under water for 1 day, followed by 3 days at 23 °C and 50 % RH before applying the hydrophobization agent. After application, the specimens remained at 23 °C and 50 % RH for 4-7 days to allow the hydrophobization agent to react. The specimens were then again submerged in water in order to continue cement hydration and to saturate the sample for subsequent NMR measurements.

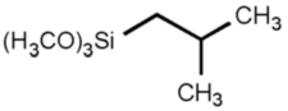
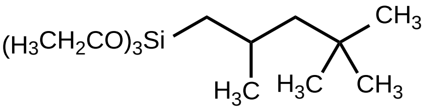
Table 1 Mixture proportions of the two types of concrete used, where OPC= Ordinary Portland Cement; PBFC = Portland Blast Furnace Cement.

Component	OPC kg/m^3	PBFC kg/m^3
OPC: CEM I 32.5 R	300	
PBFC: CEM III 32.5 R (65 % slag)		300
Water	180	
Grading curve A/B 16	180	

Hydrophobization agents

The water repellent agents selected for this study were *iso*-butyltrimethoxy silane, , and triethoxy(2,4,4-trimethylpentyl)silane (*iso*-octyltriethoxy silane), henceforth hyd.-3 and hyd.-6, respectively. The same amount of active ingredient per square metre was applied only on the unprocessed side of the specimens previously facing the mould (see Table 2).

Table 2 Chemical structure of the hydrophobization agents used in this study and details on the application.

Agent	Active ingredient	Form	Content %	Applied quantity g/m^2
hyd.-3	 *iso*-butyltrimethoxy silane	Neat	97	131
hyd.-6	 *iso*-octyltriethoxy silane	Neat	99	129

Measuring method

All presented NMR results were recorded on water saturated specimens. Water saturation was achieved by submerging the samples in water until a constant mass was reached. During this procedure, water was able to get behind the hydrophobic layer by penetrating the untreated sides of the specimen (Figure 1). The moisture profiles inside the specimens were measured by single-sided NMR and the results of the measurements are shown in the following as amplitude-depth diagrams. Hydrophobic and non-hydrophobic areas can be differentiated in terms of the observed amplitude. The amplitude itself is directly related to the number of hydrogen atoms in the measured volume. So besides water, other hydrogen containing chemical structures are also observed. However, different chemical structures can be separated by doing post processing on the signal-decay data also gained from the measurement.

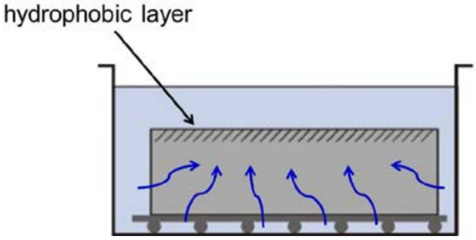


Figure 1. Specimen stored under water for saturation.

EFFECTS ON THE HYDROPHOBIC LAYER THICKNESS

Storing in alkaline solution

Both hydrophobization agents listed in Table 2 proved their stability against alkaline attack in the approved procedure for the application on concrete by the guidelines for protection and repair of concrete parts of the German Board for Reinforced Concrete [5]. Additionally to the standard test, the specimens were stored in alkaline solution for 3 months at 23 °C and for another 6 months at 80 °C. To demonstrate the accuracy of the test, specimens treated with methyltrimethoxy silane, which is known to easily undergo hydrolysis in alkaline solution and is not approved for application on concrete, were also investigated.

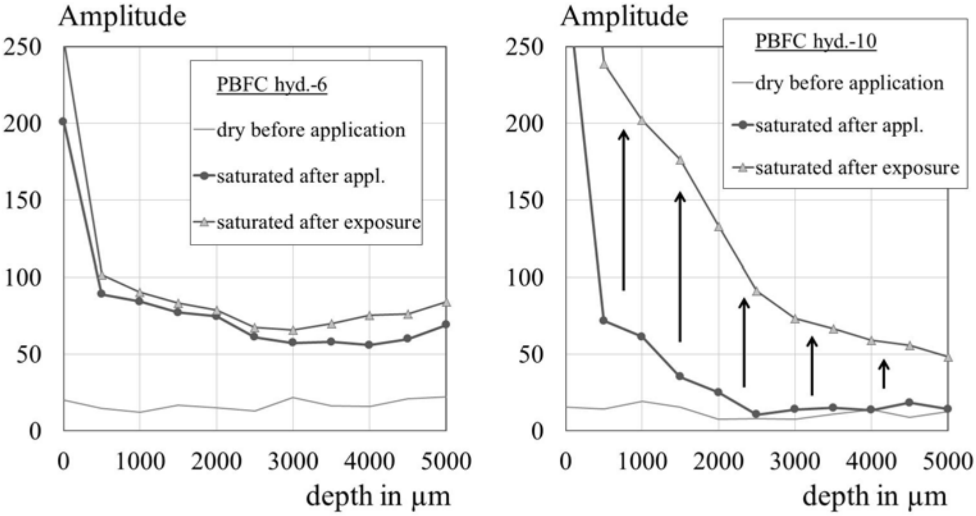


Figure 2. Amplitude-depth profile dry before application as well as saturated after application and exposure; left: *iso*-octyltriethoxy silane; right: methyltrimethoxy silane.

Even under intensified conditions both approved hydrophobization agents were unaffected by the alkaline solution. Rather, the amplitude-depth curve after exposure to alkaline media matches that of before (Fig. 2 left). After exposure, the methyltrimethoxy silane treated specimens show that water is able to penetrate into the previously hydrophobic area (Fig. 2 right). Thus, the alkalis were able to partially destroy the hydrophobic layer.

UV radiation

Figure 3 left shows a hydrophobised concrete surface that had been exposed to UV radiation for 27 days. The colour below the displayed water droplet turned dark after the droplet was put on the concrete surface. Furthermore the contact angle between droplet and concrete surface had changed from $\Theta < 90$ ° before to $\Theta > 90$ ° after exposure, i.e., the droplet is now spreading on the surface. Both effects indicate that the roll-off behaviour and the wettability of the irradiated surface changed. However, during observation the droplet remained on the concrete surface. Additionally the profiles in Figure 3 right corroborate that the UV radiation over time has no significant effect on the amplitude below the surface. Thus, the impact of UV radiation is limited to the topmost surface layers while the appearance of the hydrophobic layer inside the specimens remains unchanged. It should be mentioned that radiation which hits the concrete surface is transformed into thermal energy. However, control experiments up to 250 °C also showed no effect on the hydrophobic layer [6], which explains the unchanged hydrophobic properties of the hydrophobic layers below the surface after UV irradiation.

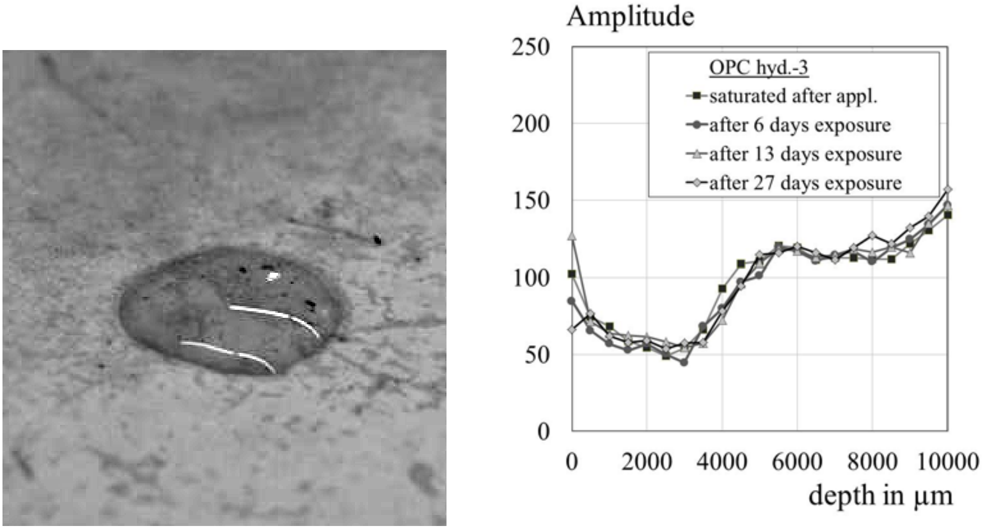


Figure 3. Left: water droplet on a hydrophobised concrete surface after 27 days of UV exposure. Right: amplitude-depth profile indicating the water distribution after different times of UV exposure.

Carbonation

There are significant differences between the results of OPC and PBFC concretes. In Fig. 4 left it is clearly shown that the carbonation of OPC based concrete has not influenced the hydrophobic layer properties. In contrast, after carbonation of PBFC concrete the amplitude between 1000 to 10000 µm increased indicating that water is able to penetrate into the previously hydrophobic area (Fig.4 right). Only a small dip in the amplitude-depth profile between the surface and 3000 µm indicates the presents of a remaining hydrophobic area.

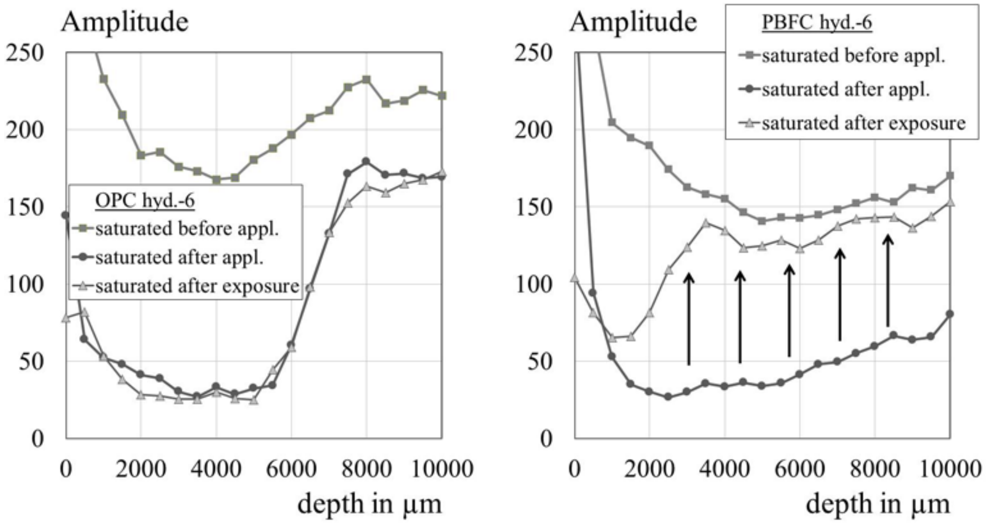


Figure 4**.** Right: moisture-depth profile saturated before and after application and saturated after expo-sure. Left: OPC concrete; right: PBFC concrete**.**

The effects on the hydrophobic layer properties can be explained by focusing on the microstructural changes caused by carbonation of OPC and PBFC concrete. In both concretes, calcium hydroxide (CH) reacts with carbon dioxide to calcium carbonate. In addition, the transformation of calcium silicate hydrates (CSH) to calcium carbonate is also possible. However, the carbonation of CH is dominant for OPC concrete due to its rather large amount of free CH. In PBFC, the amount of CH available for carbonation depends on the quantity of blast furnace slag used in the cement mixture. At a content of more than 50 wt.-% blast furnace slag, the carbonation of CSH becomes significant [7]. In addition to calcium carbonate a second solid reaction product, namely silica gel, is formed during the carbonation process of CSH. Upon carbonation, the pore size distribution of OPC based concrete shifts to smaller diameters. In contrast, during investigation the PBFC concrete reveals a shift to larger pore diameters with an increased proportion between 0.1 up to 2 µm after carbonation. This range of pore diameters is characteristic for the highly porous structure of the silica gel formed during the carbonation process of the CSH phases in the PBFC concrete [7]. In addition, this newly generated, highly porous structure is hydrophilic. Regarding the OPC results, the carbonation of CH with the resulting crystallisation of calcium carbonate has not affected the hydrophobic layer. This indicates that the formation of silica gel during the carbonation of PBFC concrete might be responsible for the effect on the hydrophobic layer properties. In contrast to the UV exposure, carbonation has no influence on the roll-off behaviour (Fig.5 left).

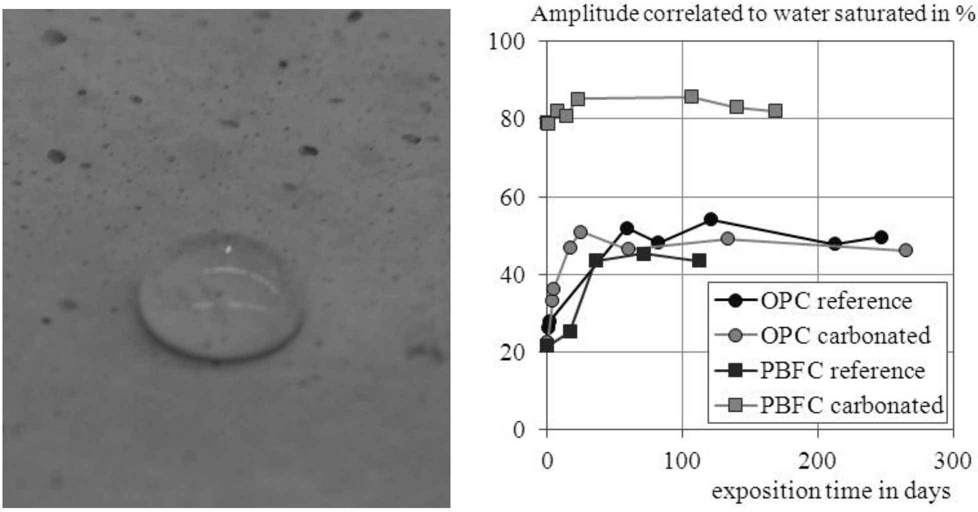


Figure 5. Left: water droplet on a concrete surface after accelerated carbonation. Right: amplitude behind the hydrophobic layer over time for OPC and PBFC specimens' reference and carbonated [8].

Additionally to the measurements on saturated specimens, the water uptake through the hydrophobic layer was also observed by NMR. For this purpose, the circumference of the specimens was sealed with epoxy resin and the hydrophobised surface was exposed to water. Figure 5 right shows the differences between the PBFC-reference, OPC-reference/carbonated and the carbonated PBFC specimen. The references and the carbonated OPC concrete are act similarly. Their results indicate that water vapour diffuses slowly through the hydrophobic area and adsorbs on the untreated pore surfaces beyond it. In contrast, the carbonated PBFC concrete showed, right from the beginning of the test, greater amplitude indicating water transport by capillary suction. After reaching the equilibrium between water diffusion/capillary suction through the hydrophobic layer and evaporationg from the unsealed backside of the specimens, a difference is found between type of water behind the hydrophobic layer. The references and the carbonated OPC concrete only showing pore surface related water while the carbonated PBFC shows additionally free water.

Hydration

Due to the higher porosity at early concrete age the requirement of active agent per volume has increased. Hence, only the topmost 4000 µm were affected by the applied quantity of hydrophobization agent (Table 2). The dip between 500 and 4000 µm in the amplitude-depth curve (Fig.6 left) observed after 3 days of water storage (7 days after application) clearly shows the presence of a hydrophobic layer. However, upon further storage under water, the dip flattens indicating increased water content in this region. Two control experiments stand in contrast to this behaviour: i) a sample that was treated with a hydrophobization agent after the cement hydration had nearly finished shows a constant water distribution over time (Fig.2 left), and ii) untreated early age concrete show a decreased water content during cement hydration (Fig.6 right).

Resubmerging the samples in water after applying hydrophobing agents restarts cement hydration and the growth of matrix-forming crystals. The latter can have two opposing effects on the water content of the hydrophobic layer and on the amplitude-depth profiles: crystals grow into the free pore volume thereby reducing the porosity and the volume available to accumulate water. This should cause a decrease in the amplitude-depth profiles as seen in the sample that has not been treated with hydrophobing agents (Fig.4 right). The surface of crystals that grow after application of the hydrophobing agent will be hydrophilic; i. e., the formerly hydrophobic pores are partially overgrown by hydrophilic surfaces. This should cause an increase in the amplitude-depth profiles and appears to be the case in the sample shown in Fig.4 left.

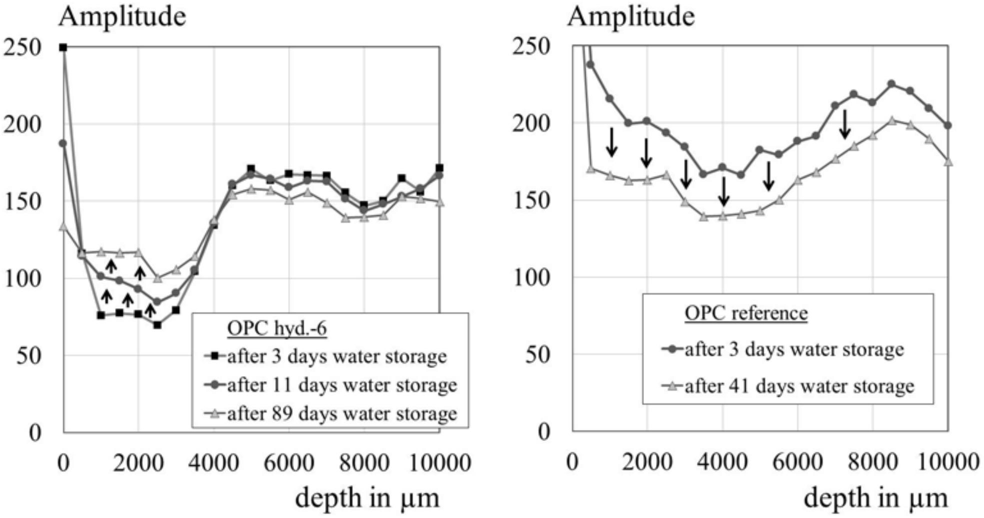


Figure 6. Left: moisture-depth profile saturated after application. Right: moisture-depth profile saturated after water storage.

CONCLUSIONS AND OUTLOOK

In contrast to their sometimes poor reputation in the field, hydrophobic layers formed by the impregnation of concrete exhibit in almost all the studied cases an excellent durability provided they were applied correctly and the original layer had a sufficient thickness. The performance of hydrophobic layers only suffers if the hydrophobization agents are applied too early, in particular, on non-carbonated PBFC. However, when implementing a hydrophobic treatment on concrete based on specialty cements, all processes acting on the treated concrete have to be taken into consideration and checked for their relevance and extent on the hydrophobic characteristics. Maintenance plans need to account for the results of these considerations in order to secure the efficacy of the hydrophobic treatment as barrier against liquid water.

The single-sided NMR method was shown to be an excellent tool for assessing the ingress of hydrophobization agents, the thickness of hydrophobic layers, and changes in the layer thickness occurring after ageing. The presented results clearly document that questions concerning the durability of hydrophobic treatments can now be answered at a much more sophisticated level. Since the NMR method used here is directly transferable to measurements on site, all investigations carried out in this study on disc-shaped lab samples can equally well be implemented directly on buildings. In the field of civil engineering, the NMR method, therefore, not only helps academia to elucidate processes relevant for the durability and performance of hydrophobic layers, but also manufacturers, contractors, and engineering consultants in assuring quality standards by detecting potential faults.

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