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Durability of Hydrophobic Treatments on Concrete – Results from Laboratory Tests

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Abstract

For many year hydrophobic agents have been used to reduce water ingress into buildings and structures. Since the applications of traditional materials in early civilizations the chemical composition of water repellent materials has been optimized. However, an estimation of their durability is not yet possible, especially in the field of hydrophobic surface treatments for concrete [1]. The main objective aim of this work was the evaluation of possible deterioration mechanisms that might lead to a loss of effectiveness of water repellent treatments and hence their durability. In order to investigate a spectrum of commercially available products, six different hydrophobic agents with different organic residues as well as different solvent types were investigated. These were applied to two different types of concrete. The specimens were aged artificially by accelerated carbonation, exposure to UV-light and high-alkaline environment. After artificial ageing different performance parameters were measured, such as contact angle, water absorption and impregnation depth. Furthermore, some samples were analyzed with the new NMR-Mouse® technology. The results show possible ways to separate different degradation mechanisms and their influences on the performance of hydrophobic treatments. The NMR-Mouse® technology reveals to be a promising possibility of measuring the impregnation depth of hydrophobic treatments non-destructively.

Keywords: concrete, hydrophobic treatment, durability, water absorption, contact angle, NMR technology

1 Introduction

One of the problems of concrete structures exposed to outdoor weathering is the ingress of water and water pollutants, e.g. chlorides and sulphates, resulting in corrosion of the concrete or even the steel reinforcement. Therefore, a reduction of the maximum water uptake can effectively be used to prevent such damages. Compared to other conservation methods, the use of hydrophobic surface treatments is one of the most simple treatments that can be applied for decreasing the water absorption of a porous material [2].

Despite the relative long time “modern” hydrophobic treatments have been used, the mechanisms which may lead to the degradation of their performance have as yet not been elucidated. Investigations of the durability are mostly based on the performance of treatments applied to outdoor structures, but in general, the important technical details about these applications are only known to a very limited extend [3].

The presented study had two main objectives: the identification of different possible degradation mechanisms; and, reproducing these in a specific laboratory setup. Then the influence of these artificial ageing conditions on the performance of hydrophobic treatments could be evaluated. The possible degradation causes were identified to be:

- Changes of the concrete pore system due to hydration and/or carbonation;
- High alkaline environment within the concrete;
- Exposure to ultra-violet light; and,
- The intrusion of dust and dirt particles into the pore system.

2 Experimental

2. 1 Materials

Two different types of concrete were used. For a rather porous substrate a C20/25 according to DIN 206-1:2001 was used. The nomenclature of this concrete is according to the compressive strength of cylindrical/cubic specimens. For a rather dense material a C040 according to DIN EN 1766:2000 was used. This concrete is used as a reference substrate for the evaluation of the performance of surface protection systems – the nomenclature refers to the w/c-ratio. All specimens were produced approx. 6 months before the hydrophobic treatments were applied and had dimensions of 20x20x6 cm^3. During that time the specimens were stored at 23°C and 65% RH. In order to avoid the influence of any organic substance, no fly ash, silica fume, superplasticizer or release agents were added to the concrete.

Table 1: Selected material properties of the two concretes

	unit	C20/25	C040
Type of cement	-	CEM I 32.5	CEM I 42.5
w/c-ratio	-	0.60	0.40
Compressive strength	N/mm²	37	63
Total porosity (Hg-porosimetry)	%	13.4	10.1
Carbonation depth 6 month after concreting	mm	~ 8	~ 3

The hydrophobic agents were delivered by a manufacturer of pure silane/siloxane products and were diluted according to the technical specifications. The active content represents the highest recommended amount specified by the manufacturer. Table 2 gives an overview of the different water repellent agents.

Table 2: Description of the hydrophobic agents

Code	Agent	active content [%]	type of solvent
A	Isobutyltrimethoxysilane	40	ethyl alcohol
B	Methyltrimethoxysilane	not determined	pure acetic acid
C	Isooctyltriethoxysilane	40	ethyl alcohol
D	Isooctyltriethoxysilane (Gel)	80	water
E	Water based silicone emulsion (secret composition)	not determined used as delivered	water
F	Potassium methylsiliconate	3	water

2. 2 Application and climatic storage conditions

Before the main test series were carried out, some preliminary tests were performed. Water repellent treatments characterized by low impregnation depths or by surface discolouring effects were excluded from further testing. The following test matrix was selected after these preliminary tests.

- C20/25 – hydrophobic treatments A through D
- C040 – hydrophobic treatments A, C and D

The hydrophobic agents E and F were excluded from the test series because they both resulted in a discoloring of the surface and agent B applied to the C040 resulted in an impregnation depth below 1mm.

The following specimens were used for the investigations:

(1) Cores drilled out of the concrete slabs with a diameter of 75mm – application of the hydrophobic agent on the original surface of the slab,

(2) Slabs (10x20x6cm³) cut out of the original specimens – application of the hydrophobic agent on the cut surface in order to treat a non carbonated surface

(3) Original concrete slabs (20x20x6cm³) – application of the hydrophobic agent on the sandblasted surface.

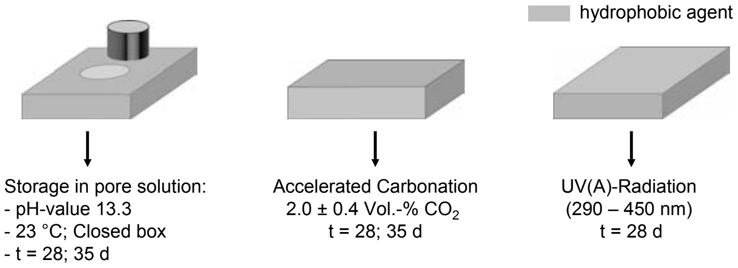


Figure 1: Overview over the different types of specimens and artificial ageing methods

The surface of the specimens (types 1 and 3) were sandblasted in order to achieve a rough texture and a reproducible surface. The surface of specimens of type 2 was cut. All hydrophobic agents were then applied by brush at 23°C and 50% RH after cleaning the surfaces with compressed air. The consumption was set to 200g/m². Afterwards the treated specimens were stored at 30 C for a week in order to accelerate the polymerization.

The different specimens were stored in different artificial ageing conditions. The temperature of all storage variations was set to 23 C:

(a) The concrete cores (1) were stored in artificial solution mimicking a concrete pore solution with a pH-value of 13.3 for 28 and 35 days. The treated surface was not covered by the pore solution, so that the transport of the alkaline solution to the treated layer was the result of capillary rise from the bulk area of the core.

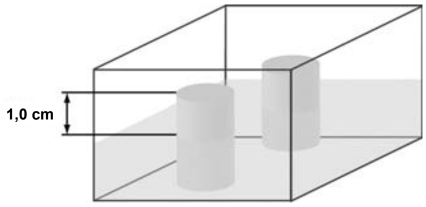


Figure 2: Storage of the specimens in a high-alkaline environment

(b) The smaller slabs (2) were exposed to air with an increased CO_2 content (2.0 v% CO_2) for 28 and 35 days.

(c) The bigger slabs (3) were exposed to ultra-violet light with a wave-length of 290 – 450 nm (UV light of this wave-length is also called UV(A) –radiation) with an intensity of approx 15W/m² for 28 days.

2.3 Evaluation methods

In order to quantify the performance change of the water repellents three different methods were used:

- Contact angle measurements, using the “contact angle system OCA” by DataPhysics. Distilled water was used as the test liquid. Each contact angle value reported is the mean of ten individual measurements.
- Capillary water absorption, on the basis of DIN EN ISO 15148. In order to ensure one dimensional water transport all specimens were sealed with a paraffin wax (except top and bottom). The water level in the basin was 5mm above the bottom of the specimens. Each mean value was determined by three single specimens.
- Impregnation depth by splitting the specimens into half and spraying a thin layer of water to the freshly broken surface. The impregnation depth of the hydrophobic treatment was then measured with a caliper gauge.

Additional measurements were performed with a NMR-Mouse®. The NMR-Mouse® (NMR-**Mo**bile **S**urface **E**xplorer) is based on NMR-technology (**N**uclear **M**agnetic **R**esonance), but is a special development of the Institute of Technical Chemistry and Macromolecular Chemistry at Aachen University with a smaller sensor in order to enable on-site measurements [4], [5]. This handheld device is a palm-size NMR sensor built with two small permanent magnets, which are mounted on an iron yoke with anti-parallel polarization to form the classical horseshoe geometry. The radio frequency field is generated by a surface coil which is placed in the gap. The measurement area of this specific NMR-Mouse® has a size of approx. 4.0cm² and a depth of 200 µm.

3 Results and discussion

Representative results obtained for the samples of C20/25 concrete will be presented. In general, the results obtained for the samples made with the C040 concrete show the same trends.

3. 1 Reference values - impregnation depth, contact angle and capillary water absorption

The impregnation depth is one of the main performance indicators for hydrophobic treatments but currently it cannot be measured non-destructively. Comparing the results obtained with the C20/25 specimens among each other, it can be seen that hydrophobic agent B shows by far the lowest impregnation depth of all. Agent B features as reactive group a methoxy group, which is more reactive than the ethoxy groups (agents C and D) or a sterically stabilized methoxy group (agent A) [5]. Consequently, the relative fast polymerization will form a hydrophobic film and not penetrate as deeply as the other agents.

Table 3: Contact angle, capillary water absorption coefficient and remaining water absorption – measured after 28 days of the water repellent application (storage until measurement at 23 C and 50%RH). The capillary water absorption coefficient for the untreated concrete (C20/25) is presented as reference and comparison.

		Reference	A	B	C	D
Impregnation depth	mm		4.5	2.1	4.9	8.2
Contact angle	°		103.1	83.6	101.	92.8
Water absorption	kg/(m^{2}h^{0,5})	0.752	0.025	0.024	0.029	0.037
Remaining water absorption	%		3.3	3.2	3.9	4.9

Comparing the other three hydrophobic treatments (A, C, and D) no direct link between the size of the molecules and the impregnation depth could be observed. The two hydrophobic agents A and C feature two completely different organic residues – A: Iso-butyltriethoxysilane and C: N-octyltriethoxysilane – but no significant difference of the impregnation depth could be detected.

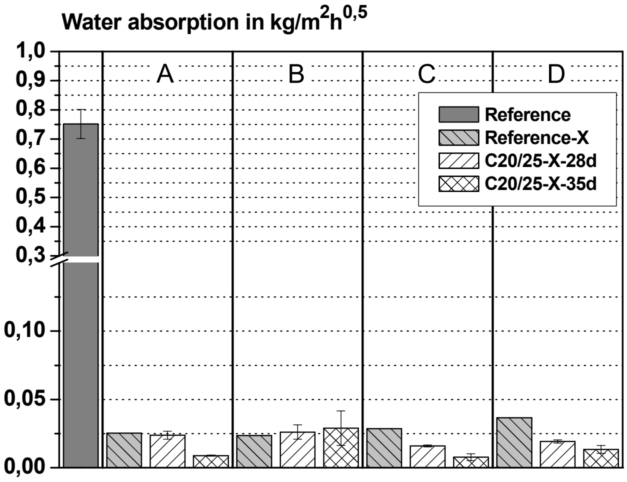
One way to increase impregnation depth is to increase the active content and/or the contact time. For example,. the active ingredient content in agent D (80%) is twice as high as that for agent C (40%), and the contact time is due to the gel-like viscosity significantly longer. Which of both factors is the dominant one, is a question that still has to be answered.

Regarding the capillary water absorption and contact angle values, it can be seen that all hydrophobic treatments produce a hydrophobic surface and are able to reduce the water absorption significantly.

3.2 Results from the artificial tests

Exposure to alkaline solutions

The artificial alkaline pore solution was not able to reach the treated surface directly (see Fig. 2) but only through capillary suction from the bulk of the concrete sample. Thus, it was not expected that the contact angle would change after this exposure and the actual measurements support this hypothesis. All specimens still show a hydrophobic surface (see Fig.3).



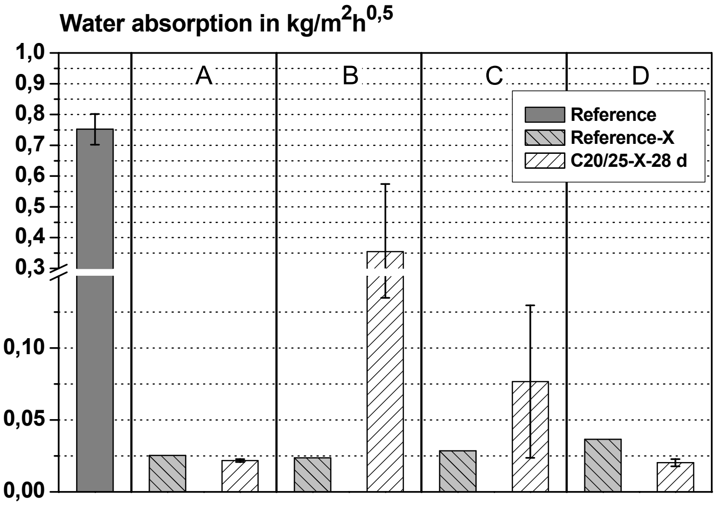
	A		B		C		D	
Exposure time [d]	28	35	28	35	28	35	28	35
Contact angle [°]	95,7	102,5	103,3	103,0	103,2	110,0	105,0	102,0
Standard deviation	6,4	8,5	8,3	10,4	9,7	9,3	9,7	9,0

Figure 3: Graph: Mean capillary water absorption coefficient of treated concrete samples after 28 and 35 days of exposure to alkaline solution; and for untreated (Reference) and treated and unaged samples (reference-x). Range in the graph gives minimum and maximum values. Table below: Average contact angle values after different exposure times with their standard deviation.

Contrary to the contact angle results, the capillary water absorption tests produced some surprising results (Figure 3). The water absorption of most of the specimens decreased (Hydrophobic agents A, C and D) after exposure. The values obtained after 35 days of storage in alkaline conditions are approximately one third of the unaged reference values. This significant decrease may be due to an increased cross-linking of the hydrophobic layer within the pore structure. This increased polymerization could presumably be monitored in a real life exposure, but it would take longer to obtain comparable results. The hypothesis of an increased polymerization is supported by the fact that agents A, C and D were especially developed for high-alkaline environments whereas agent B is supposed to work on various different porous substrates.

Influence of Ultra-Violet radiation

The influence of UV-radiation is only limited to the direct surface of the specimens, so it was expected that only the surface performance would be affected.



	A	B	C	D
Contact angle [°]	74,0	72,9	84,2	100,8
Standard deviation	8,2	9,6	8,9	8,9

Figure 4: Graph: Mean capillary water absorption coefficient of treated concrete samples after 28 days of exposure to UV-light; and for untreated (Reference) and treated unaged (reference-x) samples. Range in the graph gives mininimum and maximum values. Table below: Average contact angle values and their standard deviation

Looking at the contact angle measurements, it can be noticed that the UV(A)-radiation led to a significant decrease of the surface performance of agents A through C as evaluated by their contact angle (Figure 4). Agent D still fulfils the requirements for a water repellent surface according to the criterion that the contact angle should be greater than 90°.

Considering the water absorption coefficients, only agents A and D were not affected by UV-radiation. In the case of agent D, it is assumed that its resistance is a result of an increase of the active ingredient content and the application contact time, since it was applied as a gel. The type of active (alkyl) and reactive (alkoxy) groups apparently are not critical since agent C has the same active ingredient (n-octyltriethoxysilane) but at a lower concentration and not in a gel formulation.

The hydrophobic agents B and C show a distinct increase of the water uptake. The water absorption coefficient of agent B increases by a factor of 15 and is so approximately only half of the untreated specimen. Future studies will deal with the question of why a presumed surface change of the water repellent can lead to such a significant loss of its overall performance.

Influence of carbonation

The influence of carbonation was measured with specimens which had been stored in a high-content CO_2 (2.0 v%) environment. Additional mercury porosity measurements on small concrete cores with a diameter of 20 mm were performed after 28 days of exposure. The measurements showed that the untreated C20/25 specimens decreased their porosity by 25%. The depth of carbonation after 35 days was approximately 15mm as determined with a phenolphthalein indicator fluid sprayed on a freshly broken surface.

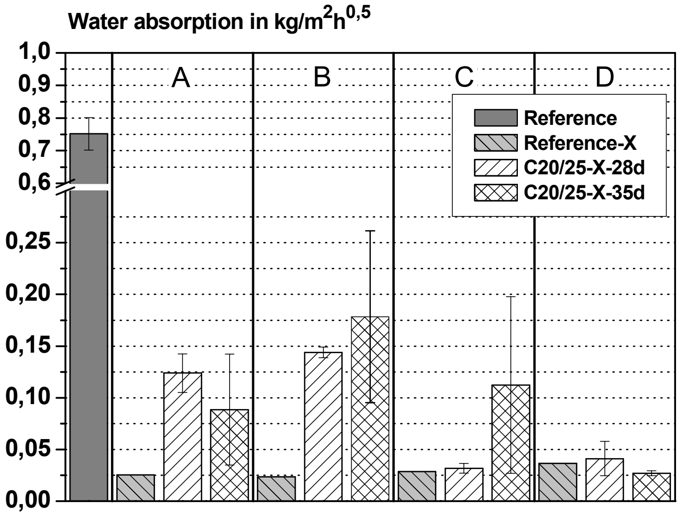
Because of the different types of surfaces (cut vs. sandblasted surface) the contact angle values measured on a cut and hence flat surface are always higher than the ones measured on a sandblasted surface. However, it can be seen that only the specimens treated with the hydrophobic agent B show a distinct loss of the surface performance – all other hydrophobic agents do not show any change of this specific performance. This leads to the conclusion that the sterically stabilized methoxy group (A) and the ethoxy group (C and D) are more resistant to the change of pore structure on the surface due to carbonation than the reactive group of agent B.

Water absorption measurements revealed not only a substantial increase of the water absorption coefficient but also an increase in the scatter of the measured values. This can be attributed to the fact that carbonation of concrete is not a locally homogenous process within the cross section.

Agent B showed the highest increase in the water absorption coefficient, in correspondence to the lower contact angle after carbonation. This could be attributed to the very low impregnation depth (2.1 mm) which was totally within the carbonation layer after 28 days exposure reflecting that hydrophobic layer is no longer effective. In what manner the hydrophobic resin is chemically or physically altered could not be detected during this study.

Only hydrophobic agent D was not affected in any way by carbonation. Once again, this could be attributed to the active ingredient content and the longer contact time.

Agents A and C, although still showing good surface performance, as measured by the contact angles, showed a significant increase in the capillary water absorption coefficient, reflecting a poor stability of the agent upon carbonation.



	A		B		C		D	
Exposure time [d]	28	35	28	35	28	35	28	35
Contact angle [°]	115,6	122,1	79,4	97,9	133,5	122,5	118,5	127,3
Standard deviation	8,2	7,4	10,5	4,5	8,2	8,3	7,5	8,0

Figure 5: Graph: Mean capillary water absorption coefficient of treated concrete samples after 28 and 35 days of exposure in accelerated carbonation; and untreated (Reference) and treated unaged (reference-x) samples. Range indicates minimum and maximum values. Table below: Average contact angle values and their standard deviation.

The study has shown that there is no direct correlation between contact angle measurements and the reduction of water absorption as already shown in a previous study.

3.3 NMR-Mouse® Measurements

The idea behind the use of a NMR technology in combination with hydrophobic treatments was to establish a measuring system, which can detect the impregnation depth non-destructively.

The first step of the study was to determine water distribution in a sample to serve as indicator of the thickness of the hydrophobic layer. A concrete core was put into water with the treated side upwards, so water penetrated through the non-treated surface from the bottom side into the concrete. The NMR-Mouse® was then applied to the treated side and the intensity of the relaxation signal was measured in 0.5mm steps. The measurements of two specimens show an impregnation depth of 2 – 3mm.

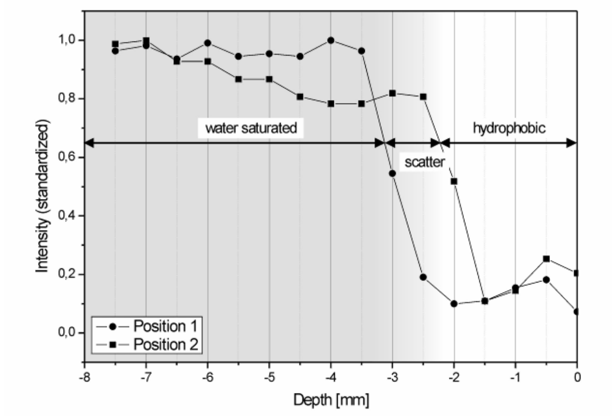


Figure 6: Standardized NMR intensity over depth indicating water saturated and hydrophobic areas in the concrete.

These preliminary results showed that the NMR-Mouse® technology is suitable to detect the effectiveness of hydrophobic treatments indirectly by the determination of water distribution within the concrete in a non-destructive way. This method could also be useful in detecting the water profile within the concrete before application of a hydrophobic agent so as to ensure suitable conditions for obtaining a sufficient impregnation depth.

4 Conclusion and future outlook

The results of the present study can be summarized as follows:

- Both types of concrete used in the study C20/25 and C040, showed similar trends. No direct influence of a high grade concrete (C040) on the performance of hydrophobic treatments could be measured;
- Two hydrophobic agents showed an increase in effectiveness upon exposure to high alkaline solution;
- The influence of the UV-radiation is limited to the surface only, but in two cases a loss of the hydrophobic performance could be measured. The reasons for this behavior are being investigated in ongoing tests;
- A change of the pore structure due to carbonation seems to affect the hydrophobic performance of water repellents substantially. The reasons for this alteration are not yet clarified;
- The NMR-Mouse® technology seems to be a suitable way to investigate the impregnation depth indirectly in a non-destructive manner.

Future research will focus on further developments of the NMR-Mouse® technology for on-site measurements. It also will be used in tests aimed to answer the questions raised in this study regarding the durability of the hydrophobic effect.

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