# Silane-based water repellent and easy-to-clean surfaces for concrete structure improvement

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## ABSTRACT

Long-term performance of concrete surfaces is one of the most important problems in the construction film. Modifications of concrete surfaces by targeted deposition of surface functional additives that make the surface hydrophobic allowed to improve the aesthetic durability of the concrete. Silane-based water repellent materials using modified silicon precursor were synthesized in a laboratory and applied on concrete substrates. The initial chemical and physical properties of the treated and untreated surface were tested at two different curing times of concrete specimens with water-to-cement ratios of 0.38 and 0.5, and using different silane-based protective systems. The longer curing time of the concrete specimens the slightly better hydrophobic effect was observed after treatment. The interactions between the applied chemical protective treatments and the concrete surface were examined. We presented a few preliminary experiments and results.

***Keywords***: silanes, water repellent surfaces, concrete treatment

## 1 INTRODUCTION

The durability of concrete structures decreases over time due to the deterioration of its constituents that are exposed to the outside environment. Most of the damage can be caused by water since aggressive agents such as chloride, sulphate, water-dissolved carbon dioxide and sulphur dioxide penetrate into concrete and react harmfully with the cement paste [1].

In addition to its civil engineering properties, concrete also has an architectural and aesthetic function. When the concrete structure ages, the visible appearance of the surface gradually changes as it is exposed to the environment, i.e. weather, pollution and biological growth. Often this aging does not take place homogeneously over the surface which combined with dirt and biological deposition of the surface reduces the aesthetic appearance of concrete. Modifications of concrete surfaces by targeted deposition of surface functional additives, e.g. with agents that make the surface hydrophobic, allow to minimize the visual aging and thus improve the aesthetic durability of the concrete. The long-lasting hybrid sol-gel systems developed and applied for plastic and metal surfaces are not always applicable to more complex concrete surfaces due to its heterogeneous, porous and rough nature.

Water repellent and easy-to-clean coatings for inorganic substrates gained strong attention during the last few years and various formulations, based on silicones or alkylpolysiloxanes besides others were developed [2]. The advantages of easy-to-clean treated materials are that dirt is easier removed. Moreover, aggressive cleaning agents are not necessary to be used for the created low energy surfaces. Water repellent effect of the substrate treated with silicones is caused by the formation of a hydrophobic organic polysiloxane thin film on the substrate, which changes the contact angle of water with the capillary surface and therefore reduces the capillary absorption. The hydrophobic polysiloxane is mainly chemisorbed on the substrate trough siloxane bonds [3].

So far, there has been few works published concerning the effectiveness of surface treatments in improving concrete durability. The effect of the protection treatment has been evaluated by testing water absorption and water evaporation [4-8], chloride permeability [6-7, 9-10] and chloride diffusion [7, 8] or water and water vapor permeability [4-5, 10]. However, there is deficiency of published literature on the performance of surface treatments for concrete with relation to the microstructure of treated concrete surface and coating-substrate interactions.

The aim of this work was to gain knowledge on the interactions between the applied chemical protective treatments and concrete surface, thereby to obtain a more fundamental understanding of the physical and chemical properties responsible for the aging of the concrete surface. The experiments were carried out on high performance concrete specimens of different composition and history, and treated with silane-based material developed in a laboratory. Moreover, the concrete specimens were treated with free different available coating systems for comparison purpose.

The initial chemical and physical properties of the treated and untreated surface were tested, i.e. hydrophobicity, surface morphology, penetration depth, adhesion. Here we presented a few preliminary experiments and results.

## 2 EXPERIMENTAL

Two concrete mixes with different water-to-cement (w/c) ratios were manufactured and examined at two different curing times. Old concrete with w/c ratio of 0.38 corresponds to 150 days of curing (O *I*) and young concrete with w/c ratios of 0.38 and 0.5 corresponds to 14 days (Y *I* and Y *II* respectively). Concrete mix proportions and compressive strength are reported in Table 1.

Silane-based water repellent materials using modified silicon precursor were synthesized and applied on concrete substrates. The silicon precursor was obtained during the hydrolysis and condensation reactions of tetraethoxysilane in the presence of hydrochloric acid (0.2 M). A homogeneous solution was stirred under reflux at 323 K for 5 h. The excess of ethanol was removed under reduced pressure. A stable sol was modified with alkylalkoxysilane to improve its hydrophobic properties and then applied with a spray pistol on the concrete surfaces.

Additionally, three different commercial products were applied on concrete substrate: solvent-free hydrophobizing alkylalkoxysilane, aqueous 'easy-to-clean' silane-based solution and aqueous 'anti-graffiti' silane-based solution. The experiments were performed on cubic concrete specimens with a size of 70×100×20 mm and 50×70×25 mm. All the specimens were treated at the same time in order to maintain the chemical and physical characteristic of the material.

The untreated and treated samples were dried at room temperature and kept in the plastic box with low humidity. The hydrophobic effect was first judged by water dropping on the treated concrete surface and the appearance of beading-effect.

The static water contact angles of various treated concrete surfaces were measured by a Drop Shape Analysis System DSA 10 Mk2 apparatus (Krüse GmbH Germany). A water drop of 5 μl from a syringe was placed on the treated sample. After the tip of the needle was separated from the drop, the CCD camera captured the side view of water drop and the contact angle was measured using a profile of the drop.

| | **O *I*** | **Y *I*** | **Y *II*** |
|---|---|---|---|
| w/c ratio | 0.38 | 0.38 | 0.5 |
| Curing time (days) | 150 | 14 | 14 |
| Cement CEM II/LL (kg/m$^3$) | 493.2 | 493.2 | 421.3 |
| Aggregate 0/4 NCC RN E 0/4 (kg/m$^3$) | 669.2 | 669.2 | 669.2 |
| Aggregate 1/4 NCC Vesterhavsral (kg/m$^3$) | 1013.6 | 1013.6 | 1013.6 |
| Superplasticizer BASF Glenium 540 (kg/m$^3$) | 5.15 | 5.15 | 2.25 |
| Water (kg/m$^3$) | 187.4 | 187.4 | 210.6 |
| Density (kg/m$^3$) | 2278 | 2278 | 2225 |
| Compressive strength (N/mm$^2$) | 70 | 70 | 46.7 |

Table 1: Concrete mix proportions and compressive strength.

For each sample, at least three measurements from different surface locations were averaged.

Microstructural features of untreated and treated samples were investigated by scanning electron microscopy (Philips XL 30) equipped with an energy-dispersive X-ray (EDX) unit.

## 3 RESULTS AND DISCUSSION

In order to have a preliminary surface characterization in terms of hydrophobicity of the treated surface, static contact angles were determined by using water as a probe liquid. The treated concrete surfaces were highly hydrophobic without any correlation with two different water-to-cement ratios of substrate.

Data presented in Table 2 show that water contact angles were ranged between 101 ° and 133 ° indicating a very low wettability with respect to probe liquid. The low values of standard deviation may be considered as evidence of high surface homogeneity and relatively smooth surfaces after treatment [11].

| | **O *I*** | | **Y *I*** | | **Y *II*** | |
|---|---|---|---|---|---|---|
| | 0.38 | | 0.38 | | 0.5 | |
| Coating system | $\theta$ (°) | $\delta$ (°) | $\theta$ (°) | $\delta$ (°) | $\theta$ (°) | $\delta$ (°) |
| Developed silane | 120 | 2 | 116 | 3 | 117 | 3 |
| Hydrophobizing silane | 105 | 4 | 101 | 2 | 102 | 2 |
| Easy-to-clean silane | 130 | 2 | 132 | 1 | 133 | 1 |
| Anti-graffiti silane | 117 | 3 | 111 | 2 | 114 | 5 |

Table 2: Water static contact angles, $\theta$ and standard deviations, $\delta$ measured for different coating systems.

Penetration depth of applied silane-based systems was preliminarily studied by scanning electron microscopy. The concrete specimens were impregnated with silver nitrate solution for 24 hours before microscopic analysis due to similarity in the composition of applied coating systems and substrates. SEM micrographs for concrete specimen treated with developed silane-based material are presented in Figure 1. We clearly observed the brighter layer of the carbonated paste in the concrete surface. The presence of dark thin layer on the top can indicate the silane-based solution penetrating the concrete specimen. However, this statement requires further investigation.

Since the aim in porous materials is mostly to prevent water penetration, the decrease in water uptake should be the criterion for evaluation of hydrophobic treatments' effectiveness. Measuring the contact angle after treatment probably can be right in a theoretical sense. If a surface is exposed to contaminants like oil or hydrophilic particles, the surface free energy is changed, so is the contact angle. However, the contamination might be only superficial, within the pores the applied treatment can be still active and the water repellency is intact. For this purpose, the treated concrete specimens were exposed to deionised water for several months.

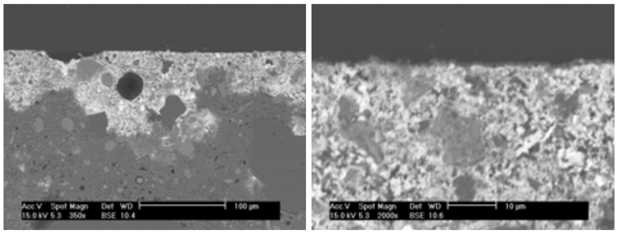

Figure 1: SEM micrographs for concrete surface treated with developed silane-based material and impregnated with silver nitrate solution.

Only the treated concrete surface was in contact with water while the remaining five sides of cubic concrete specimens were sealed with an epoxy resin. The water uptake will be investigated in our further studies.

## 4 CONLUSIONS

The concrete specimens with different history and composition were manufactured and examined. We obtained a stable water repellent solution using modified silicon precursor for concrete structure improvement. Hydrophobic effect of the treated concrete surfaces with different curing times was slightly better for older concrete specimens. The initial SEM experiments allowed to distinguish the penetrated part of the treated concrete specimen. Effect of surface treatments on aesthetic durability of the concrete surface when exposed to physical/chemical aging will be investigated. Moreover, studies of the microstructural and porosity changes of untreated, treated and leached specimens using SEM and SEM-EDX will be performed. Principle research scientist

## ACKNOWLEDGEMENT

Financial support for this research is provided by the European Research Network NANOCEM. This support is highly appreciated.

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