

## **Integral water repellent based materials: impact of aging on cement microstructure and performances.**

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### **SUMMARY:**

*Silanes and oligomeric siloxanes are increasingly used as “integral water repellent” additive for cement based materials.*

*Used at low addition levels, they enable a strong reduction of water absorption by the set cement matrix.*

*This study focused on the impact of powders based on oligomeric siloxanes, silanes or a mixture of them on the aging of the cement matrixes. Impact of accelerated aging on the cement matrix microstructure will be described. The aim is to better understand the phenomena leading to the loss of “water repellent performance” after accelerated aging.*

**KEY-WORDS:** cement materials, hydration; water repellent; microstructure; durability

## **INTRODUCTION**

Silanes and oligomeric siloxanes are widely used chemicals to hydrophobize construction materials. Surface treatment of cementitious materials with silane or oligomeric siloxane based water repellents is characterized by a relatively long durability, due to their capability to react with the cement matrix and to their excellent UV stability [1-3].

In the last 5-10 years, silane and oligomeric siloxane started to be used as an “integral water repellent”. They can be formulated as liquid emulsions or as powder additives to be used in mortar, concrete or dry mixes for the latter. A strong reduction of the water absorption by the modified cement matrix (containing these additives) is observed.

Studies of the impact of these integral water repellent products on the cement hydration processes are however limited. A previous study focussed on the cement hydration processes in the presence of oligomeric siloxane, silane or silane/oligomeric siloxane based powders [4]. However, the durability of the treatment was not assessed. In this study, the impact of accelerated aging on the protection against water penetration was evaluated, highlighting the role of the type of active agent used in the integral water repellent [5].

The influence of integral water repellent additives based on silane and oligomeric siloxane on the microstructure development of the cement matrix was investigated before and after accelerated aging.

## MATERIALS, PREPARATIONS AND METHODS

### Raw materials

Two CEM I 42,5N Portland cements (Ordinary and white Portland cement) were used in this study to prepare the mortars. Two water repellent agents,  $\alpha$ ,  $\omega$  dihydroxy-polydimethylsiloxane (PDMS referred to as oligomeric siloxane ) ( $M_w = 3000 \text{ g.mol}^{-1}$ ) and n-octyltriethoxysilane (referred to as silane) were used. Standard sand was used.

### Preparation of additives

In order to facilitate the incorporation and achieve an even dispersion of the integral water repellent additive, the pure (“neat”) silicon-based products were formulated as powdery additives. Table 1 presents the six formulations that were prepared and tested.

The water repellent based powders were prepared by spraying a 50% active content emulsion of the active materials (silane or oligomeric siloxane or a mixture of both) on a fine free powder (zeolite, an aluminosilicate with a 1.1 Si/Al ratio). The emulsions were made of silane, oligomeric siloxane or a mixture of both at a 1:1 ratio (active agent) and stabilised with a 20% solid content polyvinyl alcohol solution (PVA) (surfactant). After water evaporation, the resultant dry powder is ready to be used as an additive for dry cement mortars [6]. The powders contain 20% of active material. The raw materials used for the formulation of the powders (PVA solution and zeolite) were used as additive as well to assess their own impact.

Added in water, SHA, SHB or SHC disperse easily in water. After stirring for a few seconds, a turbid dispersion is obtained. This illustrates that the powder particles (around 200  $\mu\text{m}$ ) disaggregate, releasing in the dispersion the individual components used to make the powder formulation (the zeolite particles on one side and the emulsion on the other side).

Table 1: The six formulations studied. SH: silicon agent; A: silane; B: oligomeric siloxane and C: silane and oligomeric siloxane

Sample names	Composition
Reference (R)	no additives
PVA	PVA solution
Zeolite (Z)	Zeolite only
SHA	silane + zeolite + PVA
SHB	oligomeric siloxane + zeolite + PVA
SHC	silane + oligomeric siloxane + zeolite + PVA

### Preparation of specimens

Mortars were prepared according to EN 196-1 standard with a 0.5 water to cement (w/c) ratio with an addition of 0.5% by weight of active agents per cement mass and a 3:1 sand to cement ratio. Three round slabs (100 mm diameter and 20 mm height) specimens per water repellent tested were prepared in order to carry out water uptake tests. After demolding, the mortar specimens were stored at 20°C and >90% RH for 1 day and 20°C and 90% RH for 27 days after which they were exposed to 28 days of accelerated aging.

## Characterization methods

Water absorption of the mortars (both treated and untreated) was determined according to DIN EN 52 617. The results presented correspond to an average of three different samples.

The hydration of cement–admixture pastes was followed qualitatively by X-ray diffraction, thermo-gravimetry and differential scanning calorimetry (TG-DSC). Information concerning the progression of the hydration reactions and of the reaction products is obtained by combining these different analytical methods.

## Aging methods

Two accelerated aging methods (named as UV/T and Rain/Sun) are described hereafter.

### UV/T exposure.

UV exposure consisted in a continuous radiation of the mortar slabs for 672h (28 days) with UV light (from 290 to 450 nm) while cycling the temperature. The temperature cycle consists in: 10 hours at 40°C; cooling down to -20°C in 2 hours; 10 hours at -20°C and then heating up to 40°C in 2 hours (see Fig.1a).

### Rain/Sun cycles.

Round slabs of modified mortars were aged in a climatic chamber which can mimic Rain/Sun cycles (see Fig.1b). Cycles of 24 hours of Rain/Sun were used to artificially age the mortar slabs. A cycle starts at a temperature of 15°C that is raised at 3°C/min to 60°C. The latter is maintained for 5h and 30min. Temperature is then decreased to 15°C at a rate of 3°C/min before it is raised up again to 60°C. Rain is simulated by spraying water (1 l/m<sup>2</sup>.min) during this last 15 minutes sequence. 4 cycles of Rain/Sun comprise 24 h. Samples were artificially aged for 28 days, which corresponds to 112 Rain/Sun cycles.

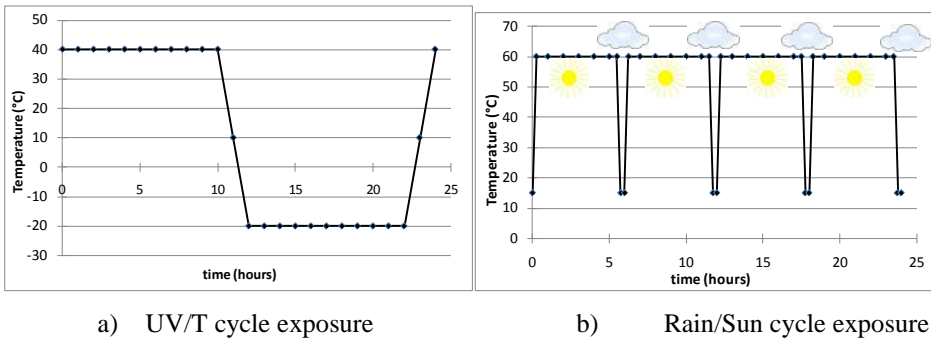


Figure 1: Evolution of temperature during a 24 hours cycle in case of UV (a) and Rain/Sun exposure (b).

## RESULTS

### Water resistance before and after accelerated aging

Capillary water absorption measurements of reference and modified mortars were carried out for a period of 48h. This specific set of results was already shared but is reproduced here for the sake of clarity in the document [5]. The mortar blocks were put in contact with water and weighed periodically. Absorption of water by the differently modified mortars was recorded as a function of time and the absorption coefficients at 24hrs were calculated.

Water uptake was determined as the ratio (in %) of absorbed water over the initial weight of dry blocks. Water uptake of mortar blocks (reference mortar -before aging-, after UV/T or Rain/Sun accelerated aging) are plotted as a function of the square root of time in Figure 2.

Before accelerated aging, reference mortars (R) and mortars modified only with zeolite (Z) absorb around 6-7% of water after 48 hours. The addition of integral water repellents leads to a strong reduction of the capillary water absorption and the capillary water absorption coefficient of these mortars is far lower.

After R/S aging, capillary water absorption of R mortar decreases. This is probably the result of densification of the cement matrix upon aging. Mortars modified with silane or silane/oligomeric siloxane (SHA and SHC) mix also absorb far less water than the reference mortar.

“Water repellent performance” is used here to describe the extent of reduction of capillary water absorption upon addition of a given integral water repellent in the mortar composition. It can then be said that the excellent “water repellent performance” of silane-based powders (SHA and SHC) are maintained after accelerated aging (Rain/Sun or UV/T).

Mortar specimens modified with PVA solution absorb slightly more water than the reference mortar. This is still the case after accelerated aging (not shown). Mortar Z specimens absorb slightly less water than the R mortar. This is still the case after accelerated aging (not shown).

The water absorption by mortar blocks modified with the oligomeric siloxane-based additive (SHB and SHC) increases after either aging tests (UV/T or Rain/Sun cycles). It is hypothesized that oligomeric siloxanes which are not anchored to the cement matrix can migrate to the mortar surface where they can be washed out by condensation water or rain. Disaggregation of the powdered additive upon addition of water during mortar preparation leads to the dispersion of individual droplets of the oligomeric siloxane in the mortar composition. The strong reduction of capillary water absorption before aging demonstrates that the droplets release the oligomeric siloxane, which can potentially migrate if it is not tightly anchored within the mortar. Oligomeric siloxanes, thanks to their low surface tension, will have a tendency to spread out on available surfaces. This can be the surface of the mortar blocs and even the surface of condensing water on it. This hypothesis should be studied further, e.g., by trying to identify diffusion of the oligomeric siloxane during the setting period of the cement since Zhang and Wittmann [1-3;7] suggested that the oligomeric siloxane agent is unevenly distributed in the matrix. It can be questioned if the increased of capillary water absorption of mortar modified with SHB after aging is due to a change in microstructure or microcrystalline composition of the cement matrix.

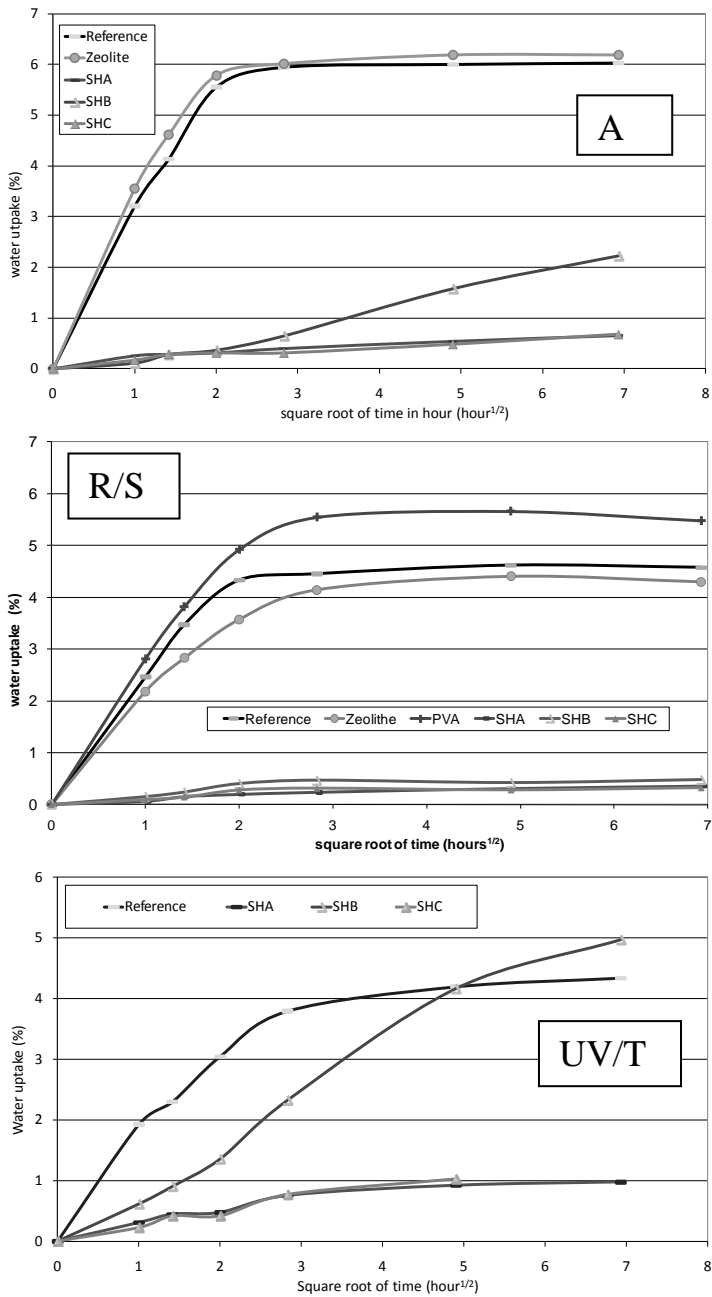


Figure 2. Effect of aging on the water absorption kinetics of the reference mortar and mortars formulated with water repellent additives for 48hrs: before aging (A), after Rain/Sun (R/S) or after UV/T aging (UV/T).

Therefore, the microstructure of cement matrix, with or without water repellent additives, before and after accelerated aging was studied. It was interesting to assess whether the changes of “water repellent performances” upon accelerated aging were coming from a change of the water repellent additives (degradation) or from a change in microstructure of the cement matrix.

## Microcrystalline composition before and after accelerated aging

The hydration of cement–admixture mortars was followed qualitatively by differential scanning calorimetry (DSC) and thermo-gravimetry as well as by X-ray diffraction. Information concerning the progression of the hydration reactions can be obtained only by combining these different analytical methods.

### Thermal analyses (TG-DSC)

The thermal analyses of reference and modified mortars were carried out and are shown in Fig.4. Between 100° and 200°C, an endothermic process due to dehydration of CSH is observed. After Rain/Sun aging, a wide endothermic peak is observed for all aged mortars. CSH obviously evolved during aging.

The dehydroxylation of the portlandite starts at a lower temperature for the aged reference, (450°C) as compared to the reference (470°C). The endotherms related to the dehydroxylation of portlandite are shifted to higher temperatures for mortars (SHB, SHC) with the oligomeric siloxane and have lower amplitude. For all compositions containing this agent, a shoulder around 400 °C is observed on this endothermic peak corresponding to the dehydroxylation.

Above ~ 600–800°C, decomposition of the carbonates occurs. Broad endothermic peaks appear in two stages for all aged mortars which should correspond to decarbonation of different carbonate compounds (calcite, carbonates of calcium aluminate and / or carbonates of calcium aluminosilicate). Beyond 900°C, calcium silicates recrystallize.

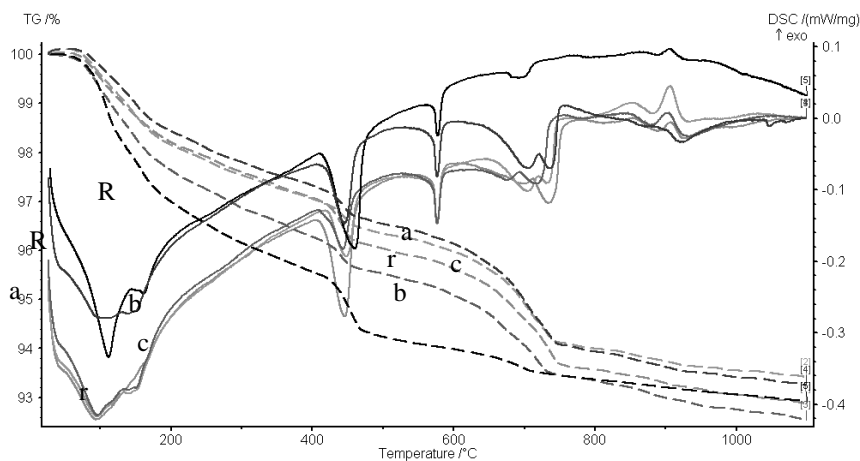


Figure 4. Thermograms of mortars studied, where: **R**= reference (before); **r**=reference after R/S aging; **c**=SHC ; **b**= SHB, **a**= SHA all after R/S aging.

## **X-ray Diffraction (XRD)**

XRD analyses were carried out on the mortar samples after curing for 28 days (Fig. 5) and exposure to accelerated aging (Fig. 6) with or without water repellent additives.

### ***Reference mortar***

The XRD pattern of reference mortar without accelerated aging (black diffractogram) is shown in Fig. 6. Quartz, portlandite (CH), mono carbo-aluminate or calcium aluminate, calcium silicate hydrate carbonates or  $\beta$   $C_2S$  phases are detected. The quartz, from sand, is detected with high relative intensity ( $s/c=3$ ). Between  $27^\circ < 2\theta < 28^\circ$ , other calcium silicate(s) are present (initial phases:  $C_3S$ ). The amount of unhydrated  $C_3S$  decreased with increasing time, as expected.

The expected crystalline hydration products are clearly evident. Some of the CH formed during initial setting can still be seen although the intensity of the peak is reduced after aging. Some calcium carbonate (Cc) is detected in aged mortar samples. The main peak of calcite ( $CaCO_3$  - Cc) appears at  $2\theta = 29.41^\circ$ , is present but with relative low intensity. The relative amounts of CH and Cc vary with the carbonation of CH, during the curing period

### ***After accelerated aging:***

Peaks due to the presence of the initial anhydrous phases  $C_3S$  and  $C_2S$  are observed after accelerated aging (only rain/sun aging presented). Between  $27^\circ < 2\theta < 28^\circ$ , the presence of calcium silicate is noticed. They do not correspond to the initial silicates phases. These might be different semi-crystalline calcium silicates such as anorthite, xonotlite and/or wollastonite, and/or some calcium silicates containing sodium ions.  $C_xS_yH_z$  gels can include many combinations of Ca/Si. Some combinations could correspond to the development of amorphous gel-like such as semi tobermorite or jennite [10-11].

### ***Mortars containing water repellent admixtures***

It can be said that the addition of water repellent does not modify the main microstructures which are formed on hydration of OPC. However, the relative intensity of CH peaks is always lower than that observed for the unmodified reference mortar. The presence of the oligomeric siloxane -based powder (SHB) does modify the height of the portlandite peak. In presence of SHB, the crystalline CH is only weakly detected after aging. This suggests that the calcium hydroxide content is similar in reference and SHB-modified mortar, although the crystal structure might be modified. This is observed from the first day of setting and is still observed after 28 days of hydration, before and after accelerated aging.

## **DISCUSSION**

One of the aims of this study was to try to understand if the reduction in performance of SHB upon aging is due to some degradation/wash out of the water repellent products itself or due to some “water repeller -induced” modification of the cement matrix (CSH gels). Maturation of CSH upon aging is a process leading to some changes of the silicate network. During natural aging, CSH gels become denser, harder and tighter, changing the CSH particles irreversibly [9]. According to Thomas et al., drying or temperature variations can cause the re-structuring of CSH gels. For example at a relative humidity  $<40\%$ , the structure collapses [8-11].

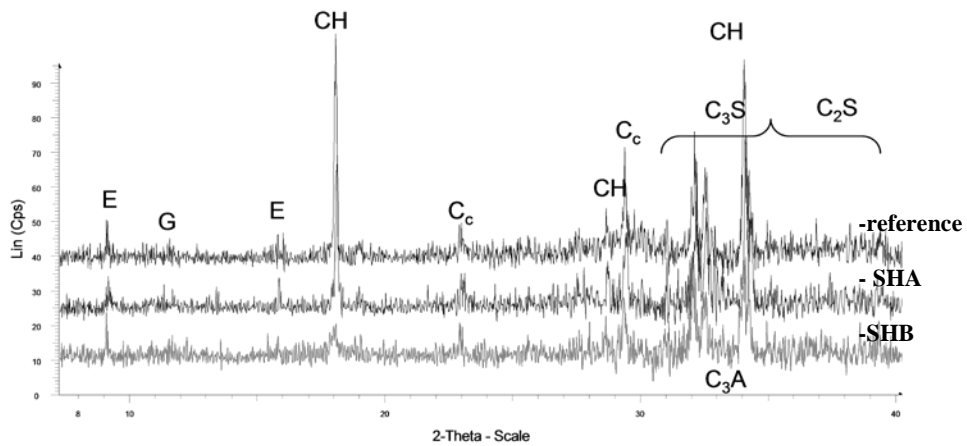


Figure 5. X-ray diffractograms of mortars containing water repellent additives and reference mortar after 28 days where E stands for ettringite, G for gypsum, CH for Portlandite and Cc for calcite.

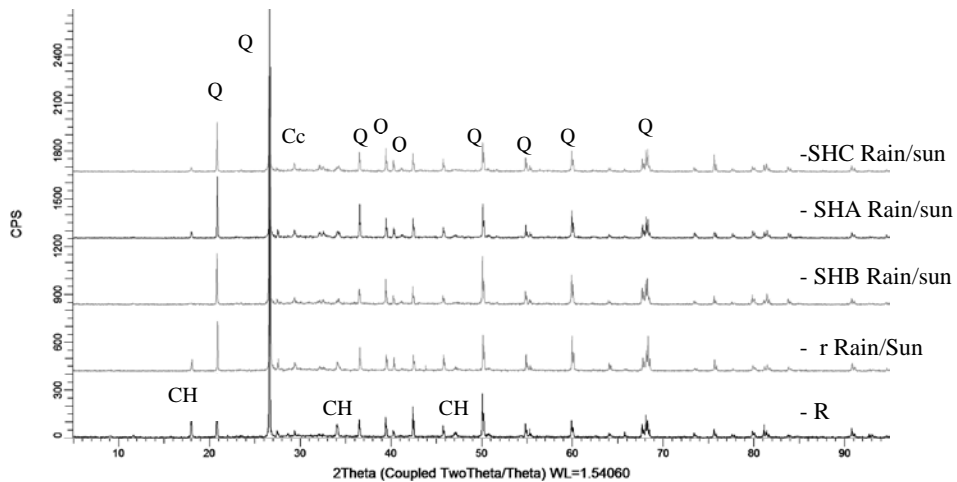


Figure 6. X-ray diffractograms of the studied mortars after Rain/Sun aging an including the reference prior to aging; where CH stands for Portlandite, Q for Quartz and Cc for calcite.

The polymerization process of the silicates chains is affected by the environment and thus impacts the evolution of the CSH gels. The polymerization can be accelerated, by increasing temperature, drying and / or rewetting. An increase in temperature, even for a short time while the hydration is taking place at room temperature, increases the degree of polymerization of the silicate network, which leads to changes in the macroscopic scale (strength and permeability). Formation of additional silicate bonds can increase the densification CSH gels [9-13]. The aging of the gels depends on the environmental

condition they were submitted to over time that may cause an increase in the degree of hydration, the polymerization and the precipitation of CSH, as well as local stresses due to changes in relative humidity and / or temperature [8-10].

It had been shown that the addition of SHA/SHB or SHC to cement paste or mortar strongly reduces the capillary water absorption of these modified compositions before any aging [4-5]. Accelerated aging leads to a significant increase of capillary water absorption of mortars modified with SHB whose hydrophobic effectiveness is almost lost upon accelerated aging. However, we could not dismiss a priori that the strong decrease of water repellent performance of SHB after accelerated aging could be due to some oligomeric siloxane-induced modification of the cement matrix (CSH gel) upon aging. Mortars modified with water repellent formulations based on silane or silane/oligomeric siloxane blends are still protected, showing low water absorption after accelerated aging. Hydrolysis of the siloxane backbone in a very alkaline environment is a known phenomenon [14]. This hydrolysis leads lower smaller oligomers that could migrate to the mortar surface and wash out thus explaining this loss of performance upon accelerated aging. The characterization of the microcrystalline composition suggests that the composition of SHB mortars is not strongly affected by the aging. The data do not support or suggest that the loss of “water repellent performance” induced by accelerated aging is due to some changes of the CSH gel or cement matrix upon aging. Rather they support the hypothesis that the loss of water repellent performance is due to the behavior of the oligomeric siloxane based water repellent itself.

Upon aging, the entire network changes with some of the “original” CSH structure being modified and new silicate chains formed. It might be argued that the new silicate structure is not “modified” by the water repellent additive, leading to the formation of new pathway for water. This assumption should lead to an increase of capillary water absorption upon aging. Integral water repellent mortars formulated with silanes (either SHA or SHC) do not absorb significantly more water after aging. They actually tend to absorb less water than before aging. The aging of the compositions containing the silane agent does not change their resistivity vis-à-vis the water penetration in their porous matrices, suggesting that the new silicate structure formed upon aging does not create preferential pathways for water absorption. Thus, these mortars are water repellent before and after accelerated aging even if they may partly react with the silicate phase in the porous CSH gel network, the final material remains integrally water repellent.

## CONCLUSIONS

The aim of this research was to study the behavior of cement matrixes modified with different water repellent formulations, before and after accelerated aging. Addition of water repellent formulations based on silane or silane/oligomeric siloxane blends in mortar decreases drastically capillary water absorption. This strong reduction is maintained even after accelerated aging, demonstrating that new silicate structure formed during aging are not providing new pathway for water absorption after aging.

Integral water repellent formulation based only on an oligomeric siloxane (SHB) strongly reduces the water absorption of the mortar, however, upon aging the protection against water penetration is almost lost. Microstructure studies carried out suggest that the oligomeric siloxane presence does not significantly affect the aging of the cement matrix, therefore, the loss of “water repellent performance” cannot be explained by a change of the

cement matrix upon aging. Consequently, hydrolysis and/ or wash out of the oligomeric siloxane based water repellent could be proposed to explain this loss of “water repellent performance” upon accelerated aging.

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