Durability of hydrophobic treatments on concrete monuments

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SUMMARY: The protection of historical concrete structures is a challenge for the coming years. Hydrophobic treatment may reduce the deterioration process while providing protection against water penetration. Existing commercial products - mainly silane or siloxane in either water or solvent based formulations – were submitted to different ageing processes including UV radiation, dry-wet cycles, thermal shocks, freeze-thaw cycles, carbonation and their effectiveness has been evaluated on the basis of contact angle, vapour and chloride permeability and, capillarity water absorption. The results obtained clearly show that hydrophobic treatments display a good behaviour under the main ageing conditions.

KEY-WORDS: hydrophobic, ageing, contact angle, UV radiation, capillary absorption, vapour permeability

INTRODUCTION

Concrete is a highly durable building and construction material though, in many cases, it is subjected to intensive environmental attack such as carbonation, chloride migration or freeze/thaw cycles [1]. For the durability and maintenance of buildings and structures, as well as for economic reasons, it is absolutely necessary to arrest or reduce these processes at an early stage where only a limited surface layer is affected [2]. However as many of these structures and buildings in Europe are already more than 50 years old, the level of deterioration of concrete has, in many cases, become a very critical problem [3]. Therefore many concrete structures and buildings require substantial repair to restore them to a working condition [4].

Concrete cultural heritage

Among building structures, concrete monuments, churches and houses are an important part of our cultural heritage and correspond to a period of architectural history which was promising and enthusiastic for the social development of humanity. Specific needs exist for interventions on historical constructions, such as respect of the original appearance, colour or texture and landscape integration, which include the use of low aggressive surface preparation techniques and selection of high quality aesthetic materials [5].

The first buildings entirely based on concrete were erected in France and Great Britain during 19th century [6, 7]. From 1906 to 1908, the apparently first concrete religious monument was built overseas [8], i.e., the Unity Temple, a Unitarian Universalist church, by architect Frank Lloyd Wright in Oak Park, Illinois: he already played with the texture and the colour of the materials, using specific aggregates [6]. This freedom of shapes would have inspired Plečnik, Slovenian architect, to select concrete as the main material for his project in Vienna: the church of the *Holy Ghost*, erected between 1910 and 1913 [9], the first church built with this material in Europe [3]. Many examples of concrete based « free » shapes exist in architecture. In the beginning of the 50's, Le Corbusier imagines a curved deck bearing on lightly inclined walls for the *Chapelle Notre-Dame du Haut de Ronchamp* (France) (Fig. 1). In San Francisco (USA), hyperbolic paraboloïds allowed architect-engineer Pier Luigi Nervi [10], with the help of architect Pietro Belluschi, to build, the tri-dimensional greek cross shape deck that covers *St-Mary of the Assumption* Cathedral between 1965 en 1970, (Fig. 2).

Figure 1. Chapelle Notre-Dame-du-Haut, Ronchamp (www.photos.igougo.com)

Figure 2. Cathedral of Saint Mary of the Assumption, San Francisco, Arch. P.L. Nervi, Photo Nicolas Janberg, Structurae 2005

More recently, emblematic concrete-based religious monument is the Gaudi's *Sagrada Familia* Church in Barcelona [11]. This, however, is a counter example of the advantages pointed out by architects: it is still under construction for more than 100 years!

Concrete has been definitively a material used not only for developing infrastructure but also for leading architectural and artistic developments [12] designed by architects and urban developers.

Hydrophobic treatment of concrete

As concrete is a porous material, it is essential to protect it against water penetration: hydrophobic treatments can provide a significant protection system. The EN 1504-2 standard defines hydrophobic impregnation as a concrete treatment for producing a water repellent surface. The inner surface of the pores is coated but the pores are not filled. No film forms on the concrete surface and appearance of the latter is slightly affected or unchanged (Fig. 3). The hydrophobic treatment will reduce the absorption of water, improve chemical resistance, reducing alkali-aggregate reaction and, if applicable, reducing chloride ion penetration.

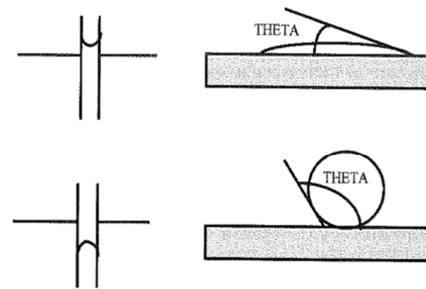Figure 3. Hydrophobic treatment principle.

Figure 4. Interaction between water and a hydrophylic (top) or hydrophobic (bottom) concrete surface.

The major objective of a hydrophobic treatment is to increase the contact angle of water (Fig. 4) and reducing surface free energy of concrete or mortar [13]. According to the equation of Young-Dupre (eq. 1),

$$(\gamma_S - \gamma_{SL}) / \gamma_L = \cos \theta \qquad \text{(equation 1)}$$

where γ_{SL}, γ_L and γ_{SV} are the interfacial free energy and the surface free energy of liquid and solid into contact with liquid vapour, respectively, and θ the contact angle (Fig. 4): if θ is increasing, it means that $\cos \theta$ is decreasing. As γ_L is constant, it means also that γ_S is decreasing.

With increasing contact angle, less wetting of the surface will occur.. Moreover, it will not penetrate the pore system of concrete if the surface of the pore has been treated: absorption forces become repulsion forces and water is "expulsed" from the surface [14].

The most common products belong to the silane family. Various kinds of silanes result depending on the different alkoxy or alkyl groups linked to the silicon atom. These products do not act all in the same manner (Fig. 5): in general, the larger the molecule of the alkyl group, the better the water repellency of the silane.
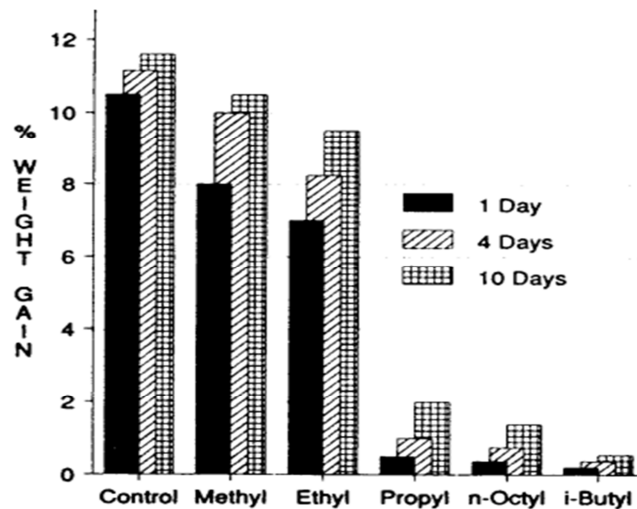

Figure 5. Influence alkyl group type on the hydrophobic efficiency of a silane [15].

Some products induce hydrophobic film formation that badly resists in alkaline media (even if alkalinity was necessary for the initial reaction). Some silanes with alkoxy groups may polymerize if, during the application, they come into contact with water and may hydrolyse: they lose their penetrating power and cannot react with the concrete [16]. The silane molecules are very small (10 to 15 Angstroms) and can penetrate even a very dense concrete, applying additional layers if necessary. Penetrations of more than 5 mm in concrete [17] are observed. The water repellency of concrete treated with silanes has been found to be still effective after 35 months exposure to outdoor climate: these products have durable effect on water absorption [17].

A second group of this family is constituted by oligosiloxanes. Siloxanes react with the silica contained in the concrete to form a hydrophobic layer. Siloxane molecules are oligomers and therefore larger than the silane molecules (25 to 75 Angstroms). These products cannot penetrate as deeply into the surface and may not be appropriate for the protection of dense concretes.

In this research project, existing products – mainly based on silanes and siloxanes were subjected to different ageing processes including UV radiation, moistening cycles, thermal shocks, freeze-thaw cycles and carbonation and efficiency has been evaluated on the base of contact angle, capillarity absorption, vapour and chloride permeability.

EXPERIMENTAL

Materials

The concrete formulation was prepared following standard "NBN EN 1766" using CEM I 52.5 and W/C ratio of 0.7. Six batches were prepared with the same mix; each one produced five slabs (40x40x8 cm). Each slab was cut into four samples of 20x20x8 cm; 8 cm cylindrical samples were cored into slabs for permeability, capillary absorption and chloride ion diffusion tests. All samples were stored for 28 days in a humid chamber (90% RH); and then they were placed in a chamber at 23°C and 60% relative humidity for drying before applying the hydrophobic treatments.

As the study focuses on the durability of hydrophobic treatments on existing concrete structures, only penetrating water-repellents were tested. The products selected correspond to those in used in North Western Europe climate conditions. Duplicate sets of samples were treated with either of two products: the first, a water-based repellent commercial product. The data sheet defines it as an alkyl alkoxy silane product, henceforth

referred to as "water based". The second product was a siloxane resin an alcohol based solvent, henceforth referred to as "solvent based". The hydrophobic treatments were brushed on to the surface of the samples, following the recommendations of the manufacturer. The studied face is the smooth "mold face". This side is intended to represent the external wall of a building.

Methods

Permeability to water vapour

The water-vapour transmission rate was evaluated according to the dish method for free films, following to the ISO 7783 standard [20]. This test uses a difference in relative humidity between the two faces of a sample. The water-vapor permeability rate is determined as a function of the amount of water vapor which passes through the specimen. For this test, cylindrical samples of 8 cm diameter and 3 cm thickness were prepared. The lateral faces were waterproofed with epoxy resin. The sample is set on a glass cup and the edges are sealed with wax in order to reduce moisture transfer to only one direction. A saturated solution of potassium nitrate KNO_3 guarantees a relative humidity of 93.2% in the cup. The device is placed in a conditioning chamber where the relative humidity is 60% at 20°C. The thickness of the equivalent air layer is evaluated.

The standard proposes also a classification of samples in three classes by water-vapor transmission

Table 1: Classification by water-vapor transmission equivalent layer

Class	S_d (meters)
High (I)	<0,14
Medium (II)	0,14 to 1,4
Low (III)	> 1,4

Capillary absorption

The measurement of the liquid water transmission coefficient **w** was carried out following standard EN 1062-3 [21] after ageing. Cylindrical samples with a diameter of 8 cm and different of heights were prepared. Only one face is treated with water-repellent, the others are waterproofed with epoxy resin. The treated face is immersed in 5 mm water and the sample is weighed after 1h, 2h, 3h, 6h and 24h. The coefficient of water-liquid permeability **w** is calculated from the slope of the linear part of the curve.

Table 2: Classification by liquid water permeability

Class	Liquid water permeability w ($kg/m^2h^{0,5}$)
High (I)	> 0,5
Medium (II)	0,1 to 0,5
Low (III)	<0,1

Chloride ions permeability

An accelerated chloride permeability test was performed. This test followed standard ASTM C 1202-97 [22]. The test principle is to apply a 60V current passing through the sample. The sample is in contact with both cells through the railings. One cell contains a 0.3 M NaOH solution and the second a 3% w/v NaCl solution. The positive terminal of the generator is connected to the NaOH reservoir and the negative terminal on the NaCl one (Fig.6). The test consists in measuring the intensity of the current generated by a constant voltage of 60V maintained for 6h. The current induces the Cl$^-$ in the sample to move towards the positive terminal; the more chloride ions pass through the sample and the higher the current. The amperage is measured every 30 minutes for 6 hours.

Core samples of 8cm diameter and 5cm thick were used. The lateral faces of the samples were covered with epoxy resin. Before testing, the samples were immersed for one week in a solution of NaOH for saturation
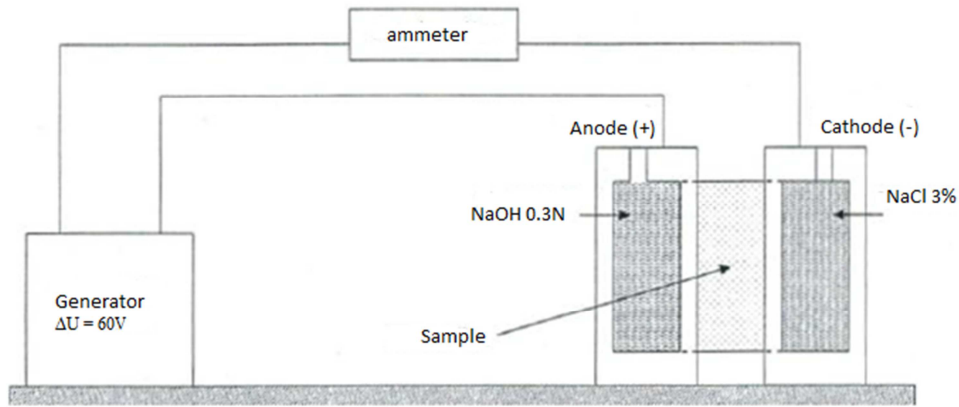
Figure 6. Diagram of the electrical assembly for chloride ion permeability.

Following ASTM 1202-97 recommendations, the electric charge passing through the sample can be determined as follows:

$$Q = 900 \ (I_0 + I_{30} + I_{60} + \cdots + I_{300} + I_{330} + I_{360})$$

Where I_i is the amperage after i minutes.

This equation is valid for sample with a section of 95 mm. A correction is needed:

$$Q^* = Q \times (\frac{3.158}{3.75})^2$$

Q^* is the electric charge passing through a sample of 50mm (3,158 in) of diameter.

The standard proposes a classification of samples according to their chloride ions penetrability.

Table 3: Chloride ion penetrability based on charge passed (ASTM 1202-97)

Charge Passed (Coulombs)	Chloride Ions Penetrability
> 4000	High (I)
2000-4000	Moderate (II)
1000-2000	Low (III)
100-1000	Very Low (IV)
<100	Negligible (V)

Contact angle measurement

A water drop is placed with a computer-assisted syringe on to the sample surface. The contact angle between the hydrophobic surface and the droplet of water (Fig.4) is measured by a CDD camera linked to the computer.

Accelerated ageing

UV light exposition

To simulate the deterioration process caused by sunlight, the samples were placed in a chamber to expose the treated face with UVA lamps. The lamps are electrically equivalent to an ordinary 40-watt fluorescent lamp. It provides a simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cut off of 295 nm. Its peak emission is at 340 nm. This device provides cycles of 4 hours of UV exposition followed by 4h of condensation, for a total duration of 700 hours.

Freeze/thaw cycles

The samples were exposed to 20 freeze/thaw cycles. For each cycle, the samples were immersed for two hours in salted water at -15°C then immersed in water at ambient temperature for two hours. Just one surface is exposed, while the others are sealed with epoxy resin.

Thermal shocks

Each sample is exposed to infrared lamps (245V, 250W) and a water-jet in a storm simulation tank; the face of samples offer slight inclination of about 3° (relative to the horizontal) to allow water to flow quickly. The surface temperature can reach up to 60°C. For each cycle, the samples are exposed to infrared lamps for 5h 45min and then sprayed with water at 12°C for 15 minutes. The samples are exposed to 20 freeze/thaw cycles followed by 10 heat shocks cycles. Tests were performed on the same samples that underwent freeze/thaw cycles.

RH cycling

For this test, the six faces of the 20x20x8 cm samples were treated with one or the other hydrophobic agents and four samples for each agent were tested. The test consists in exposing the samples to different relative humidity: each cycle lasts for two weeks: the samples are first stored in an atmosphere of 90% RH (for 1 week) and then 50% RH (for 1 week).

Carbonation

The resistance to the carbonation process induced by the applied hydrophobic agent was also assessed. The samples are exposed to carbonation for one month. The conditioning chamber contains a gaseous mix with a CO_2 concentration of 50% (v/v) and a 60% RH. The space in the chamber is limited, and small samples (20cmx8cmx8xcm) were used. The hydrophobic agent was applied on the six faces.

RESULTS

The wettability of a surface is directly related to the value of the contact angle between the water droplet and the solid. The contact angle evolution after ageing is given in Figure 7. The contact angle for untreated concrete is below 50°. We note that, before ageing, the products meet already requirements, especially siloxane treated, which leads to superhydrophobic behaviour (145°). The obtained data show that even after subjected to artificial ageing, the products keep their hydrophobic performance. Nevertheless, in two cases, the products lose their performance reaching angles below 90°: the water based product with UV light exposure and the solvent based with the thermal shocks cycles. Considering this parameter, the effectiveness of the solvent based product treatment is better than that of the water based product.
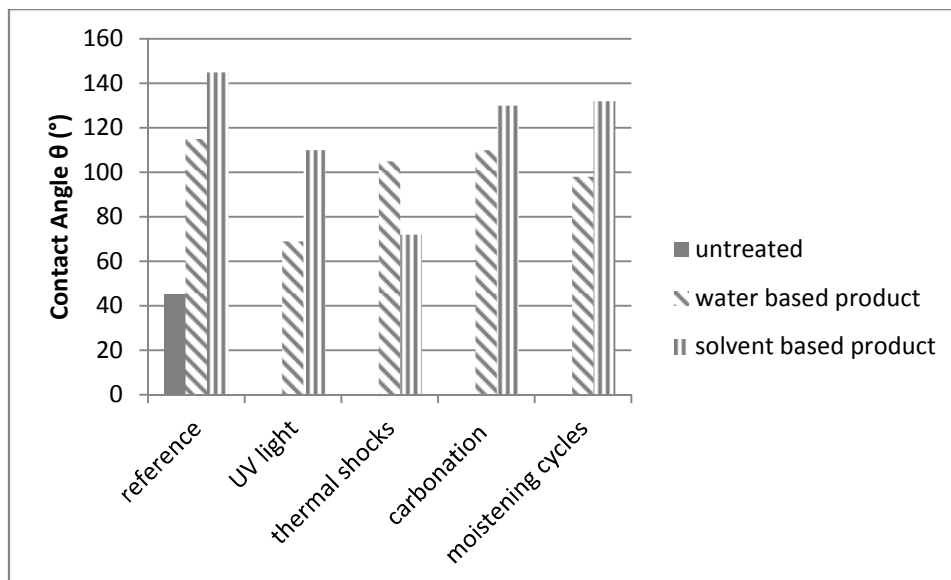

Figure 7. Water contact angles after ageing.

The influence of UV light ageing was evaluated only by the resistance to chloride ion penetration (Fig. 8). Before ageing, both untreated and treated samples present moderate chloride ions permeability (II). The values are between 2900C and 3900C. After UV lights treatments, the chloride penetration resistance is critically diminished by almost twice as much for both water-repellents. For the solvent based product, the corrected charge increases from 2914C to 4910C, and for the water based product from 3446C to 6007C. The treated

concretes fall then into another classification group (I) and present a high level of chloride ion penetrability. The solvent based product is more efficient against chlorides penetration than water based product before ageing and after UV treatment.
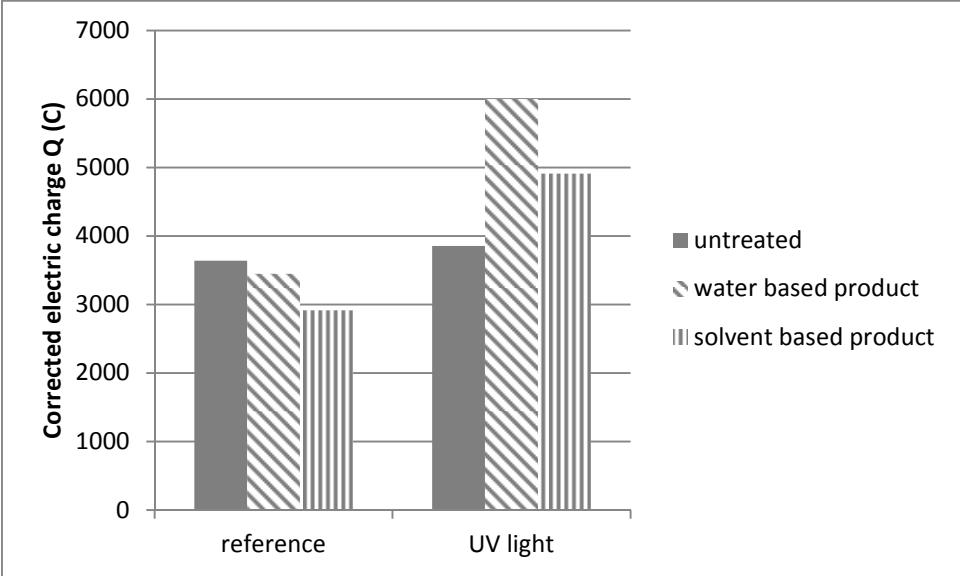

Figure 8. Chloride ion penetration before and after UVA exposure.

The efficiency of hydrophobic treatment on water absorption reduction is evident (Fig. 9). The value decreases from 0.112 $kg/m^2h^{0,5}$ for untreated samples to 0.0405 $kg/m^2h^{0,5}$ for solvent based product treated and to 0.0058 $kg/m^2h^{0,5}$ for water based product treated sample. The water based product seems to be more effective as the **w** coefficient has a ten-fold decrease compared to sample treated with solvent based product thus significantly reducing water penetration.

Most ageing processes slightly degrade the effectiveness of water-repellent with regard to water permeability, but without compromising their performance. In fact, for every ageing process except thermal shocks, the sample remains in the low permeability class (<0.1 $kg/m^2h^{0,5}$).

For the water based product, the coefficient of water-liquid permeability stays at a low value (0.05 $kg/m^2h^{0,5}$) for each ageing process except for thermal shocks. After this ageing, the surface of the water based product treated sample was badly degraded which explains the high coefficient measured after this ageing. On the other hand, the solvent based product treatment offers a good resistance to ageing exposure and stays in the low class permeability.
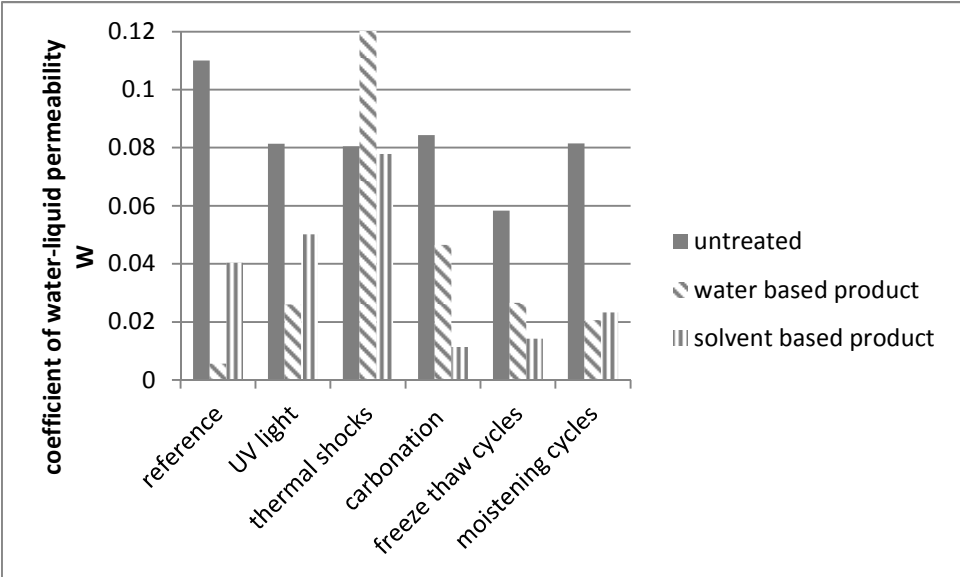

Figure 9. Coefficient of water-liquid permeability w after ageing

Before ageing, a hydrophobic treatment doesn't seem to have any influence on the water-vapour permeability (Fig. 10). The values of treated samples are close to that of the untreated sample (3 m for untreated, 3.6 m for water based product and 4.3 m for solvent based product treated, respectively). The values of equivalent layer of aged sample are in the same order of magnitude and show a low variation. For each sample after ageing the class of permeability is quite low. The resulting variations are certainly due to a "sampling effect" and probably resulted from the natural variation of the concrete.
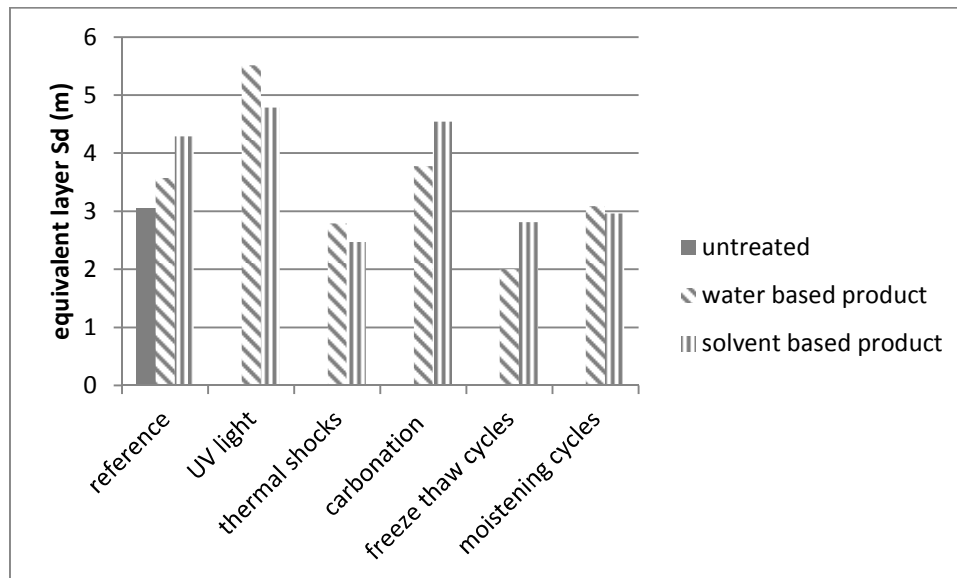

Figure 10. Water-vapour permeability after ageing.

CONCLUSIONS

In order to reduce the natural deterioration of concrete used in cultural heritage buildings, the durability of two water-repellent agents was assessed after various artificial ageing exposures. Five ageing processes were applied on concrete samples treated with the water-repellents and the changes of the measured properties assessed.

Thermal shocks and UVA exposure are the most critical ageing process: UV light may break the Si-O-Si bonds of solvent based product molecules at the surface of the concrete; however, molecules that penetrated into it may remain intact.

The hydrophobic treatments tested showed a very low influence on the water-vapour permeability. The variations in the data probably come from a sampling effect. Such treatments do not prevent the transfer of moisture in and out of the concrete.

Regarding the water-liquid permeability and the contact angle, as expected, the products offer a very good behavior and improve the permeability class. They resist very well to ageing processes and don't lose effectiveness.

The solvent based product tested is more effective than the water based product. It offers better intrinsic properties and is more durable regarding laboratory ageing. Moreover, only the solvent based product remains stable and neutral from visual color inspection after undergoing different ageing procedures. The nature of the solvent can be an explication. The solvent based product uses an alcohol solvent which is more effective than the aqueous solvent, but is less appealing for ecological considerations.

The application of a solvent based product based hydrophobic treatment has an important influence in reducing concrete deterioration and can be a solution for the preservation of cultural heritage that uses this material. It reduces water penetration into concrete and remains effective even when weathered. However the combination of several ageing factors may affect its durability. This can be remediated by periodical reapplication of these treatments thus avoiding their loss of performance over time

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