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Which Factors Influence Most the Durability of Water Repellent Treatments: Stone Properties, Climate or Atmospheric Pollution?

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Abstract

In the study, four types of water repellents, commonly found on the market, were evaluated on seven lithotypes of Champagne-Ardenne monuments. The combined impact of urban atmospheric pollution, climate and stone properties on the water repellent efficacy was assessed, allowing a better understanding of the durability of the treatments.
For six years, stone samples were exposed to outdoor environment on upper locations of both the Reims and the Langres cathedrals. These two monuments experience different environments. In Reims, atmospheric pollution is mainly linked to road traffic and urban environment and, because of the cathedral's location, the climate is slightly continental. In Langres, the level of pollution is lower, but the climate is more extreme with numerous freezing cycles.
The evaluation of the treatments' durability was assessed through various laboratory measurements. The behaviour of the water repellents depended mostly on the stone types as well as the environment to which they were subjected.

Keywords: water repellent, durability, limestone, natural ageing.

1 Introduction

The monuments of the Champagne-Ardenne district, in the north-east of France, were built with a great variety of limestones, coming from different places and having very diverse aspects and properties. In the past, when important deterioration was observed on the stones, these were replaced. However, lots of quarries are closed and it is presently difficult to replace stones from the monuments with the same kind [1]. Since the 1970's, with the increasing concern for conservation, protective and consolidating treatments have been applied on monuments during restoration works to protect them from further weathering.

The durability of water repellent treatments is usually considered to range between 5 and 10 years [2], although some applications proved to be still efficient after 24 years [3]. Nonetheless, the success of a treatment does not depend on the treatment alone, i.e. the product and its application, but also on the substrate to which it is applied and the environment to which it is exposed [4]. In fact, there is a lack of knowledge concerning the durability of water repellent treatments in-situ, as their evaluation is primarily carried out in the laboratory [5]. Furthermore, in many instances only artificial ageing tests have been carried out. Water repellent treatments are often applied on monuments with little information about their ageing and their durability in an outdoors environment [6].

To fill this lack of knowledge, a programme of exposure was initiated by the Laboratoire de Recherche des Monuments Historiques in 1998. The aim was to study the impact of climate and atmospheric pollution on the efficacy and durability of water repellents applied on limestones from the Champagne-Ardenne area [7]. During the period of exposure, climatic data and rainwater analyses were recorded to characterise the environment. After 6.5 years, the stone samples were taken to the laboratory to test the residual efficacy of the water repellents. The paper evaluates the results of the tests carried out taking into account to the environmental conditions to which the samples had been subjected.

2 Experimental methodology

2.1 Tests

2.1.1 Colour measurements

Colour measurements were performed on the samples before and after exposure with the Minolta Chroma Meter CR110, with a 50mm diameter measuring area, using the CIE system. The measurements were performed in the laboratory after conditioning the samples at 20°C and 58 % relative humidity (RH).

The values for L*, a*, b* are the average of three measurements performed on the treated surface. The difference of lightness ΔL* is the difference between the luminance L* after exposure and the luminance before exposure L^*_0. The global colour difference ΔE* is calculated according to the following equation:

$$\Delta E^* = \sqrt{(L^* - L^*_0)^2 + (a^* - a^*_0)^2 + (b^* - b^*_0)^2}$$

2.1.2 Microdrop (according to RILEM Test n°II.8b)

Microdrop absorption was used to assess the water repellent properties of the outermost zone. Drops of 5 µl were used for the test. The contact angle (θ) between the microdrop and the substrate indicates the water repellency of the substrate surface. When the contact angle exceeds 90°, the surface is said to be hydrophobic. A simple measurement of the contact angle is obtained by naked eye estimation. Five classes were determined according to Figure 1.

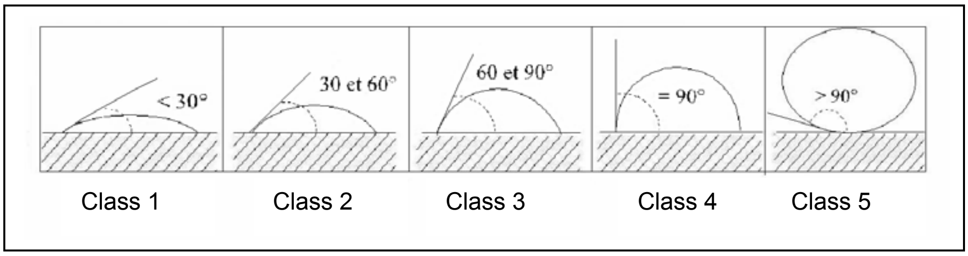

Figure 1: Contact angle classes.

2.1.3 Capillary water absorption coefficient (European standard EN1925)

While microdrop absorption provides information on water absorption by the stone surface, the capillary water absorption characterises the capillary water uptake by the stone. As the water repellent acts as a barrier against water penetration, the capillarity of treated stones is significantly reduced.

The treated top face of the cubes was put in contact with water. The stone samples were weighed at regular intervals up to 96 hours.

The water uptake coefficient W [$kg.m^{-2}.h^{-1/2}$] represents the initial amount of water absorbed per square meter as a function of the square root of time.

2.2 Stone materials

The limestones selected for this study are typical of monuments and official buildings in the Champagne-Ardenne district. Four of them are quarried in the region: Courville, Savonnières, Langres stones and Champagne chalk, whereas Jaumont stone, coming from another area (Lorraine), is very similar to the Dom-le-Mesnil stone, located in Champagne-Ardenne but not longer quarried. The Charentenay stone is used as a replacement stone for the Champagne chalk in restoration works.

These limestones represent a wide range of petrophysical characteristics that are summarised in Table 1. The porosities vary from 7.4 % to 42.5 %. The most porous one is the Champagne chalk, which also shows a high capillarity and permeability to water vapour. Three of them, Courville and Charentenay stones and the Champagne chalk, are susceptible to frost damage, as their saturation coefficients are higher than 85 %, according to Hirschwald classification [8]. Langres stone is very different from the others. Its porosity and water absorption are very low, while the mean pore diameter is very high.

These variations are linked to petrographical differences: Courville and Charentenay stones and the Champagne chalk are fine grained limestones, mainly made of micro-crystalline calcite (micrite) whereas Savonnieres, Jaumont and Langres limestones are mostly composed of larger elements (oolites, skeletal grains, etc.) and macro-crystals (dolomite and calcite crystals).

The stones were cut in cubes of 7x7x7 cm^3.

Table 1: Petrophysical properties of the limestones

	Total porosity (%)	Water uptake coefficient ($kg.m^{-2}.h^{-1/2}$)	Saturation coefficient (%)	Mean pore diameter (µm)	µ-value (Water vapour permeability)
Courville (CO)	21.5	1.8	90.9	0.2	33.3
Savonnières (SA)	32.4	1.4	48.2	1.0	27.0
Chalk (CR)	42.5	21.1	96.4	0.6	10.5
Charentenay (CH)	24.4	7.9	90.8	0.7	21.8
Jaumont (JA)	19.3	1.0	74.8	0.9	101.9
Langres (LA)	7.4	0.8	51.5	9.9	127.5

2.3 Treatments

The water repellents selected correspond to four chemical families, marketed in France: an alkylpolysiloxane in solvent (Rhoximat H224 from Rhodia), an alkylpolysiloxane in aqueous emulsion (VP1311 from Wacker), a silicone resin in solvent (DF104 from General Electric), and an acrylic emulsion with Teflon (IMLAR CPC 1175T from Doerken).

The stone cubes were treated with the water repellents on all faces, following the recommendations of the technical data sheet (Table 2).

Table 2: Treatment conditions

Product	Dilution (v/v)	Solvents	Application technique
Imlar	50 %	Water	Paint roller, repeated two times
H224	10 %	White spirit	Brush until no more product is absorbed
DF104	10 %	White spirit	Brush until no more product is absorbed, repeated two times
VP1311	6 %	Water	Brush until no more product is absorbed, repeated two times

The samples were conditioned for four weeks in a laboratory at controlled temperature and relative humidity (20°C, 50 % RH) and subsequently for a month in a chamber at 22°C and 58 % RH.

To determine the depth of penetration of the water repellent products, the limestone cubes were cut in half and then soaked in water. The penetration depth was measured on the freshly cut surface as the borderline of “wetness” was clearly visible. No measurement was made for the acrylic product Imlar, as it is a film-forming water repellent.

The results obtained for H224, DF104 and VP1311 are displayed on Figure 2. The micro-emulsion VP1311 shows a very low penetration, between 0.5 and 1 mm, regardless the stone type. On the other hand, H224 and DF104 present a higher penetration, especially in the porous and capillary stones such as Charentenay and Champagne chalk.

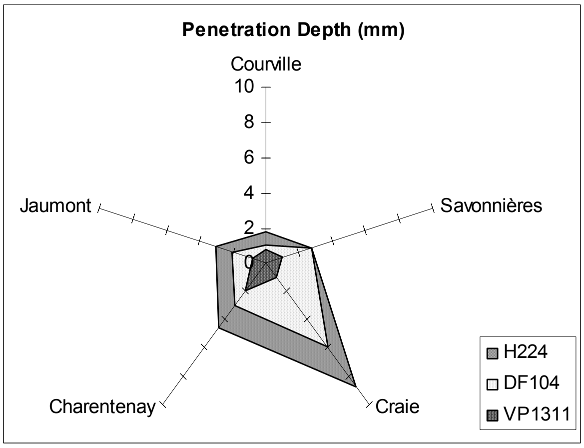

Figure 2: Penetration depth of the different products applied to the various limestones.

The evaluation of the treatment was carried out following the recommendations of Sasse and Snethlage [9]. A treatment is considered to be good if:

1) The water uptake coefficient W is lower than 0.1 $kg.m^{-2}.h^{-1/2}$;
2) The contact angle (θ) is higher than 90° (corresponding to class 5);
3) The increase of the water vapour diffusion resistance coefficient (μ) is lower than 20 %;
4) The global colour difference (ΔE) is lower than 3.

These four properties were measured on the samples and the results are displayed in Table 3, where the black background is used for values that do not fit the recommendation. The raw values are not taken into account in this specific study.

Table 3: Evaluation of the treatment applied on limestones: Capillary water absorption coefficient, W [$kg.m^{-2}.h^{-1/2}$]; classification of contact angle, θ (see Fig.1); % increase of water vapour diffusion resistant coefficient, μ; and global colour difference, ΔE. (n.d. : not determined)

	Imlar				H224				DF104				VP1311			
	W	θ	μ	ΔE	W	θ	μ	ΔE	W	θ	μ	ΔE	W	θ	μ	ΔE
CO	n.d.	4	31	3,1	0,1	5	20	3,4	0,1	5	n.d.	3,2	0,3	5	14	4,1
SA	n.d.	4	28	8,0	0,1	5	65	4,9	0,1	5	25	5,1	0,1	5	65	6,3
CR	n.d.	4	87	5,1	0,1	5	88	3,3	0,1	5	18	3,1	0,1	5	101	2,9
CH	n.d.	4	63	2,7	0,1	5	19	5,8	0,1	5	9	5,4	0,1	5	10	4,5
JA	n.d.	4	18	2,6	0,1	5	-17	4,7	0,1	5	-34	6,5	0,2	5	-15	5,2
LA	n.d.	4	10	n.d.	0,4	5	-31	n.d.	0,1	5	85	n.d.	0,1	5	196	n.d.

2.4 Sites and exposure

The stone sets were installed on two monuments: the cathedral of Notre-Dame in Reims and the Cathedral of Saint-Mammès in Langres, in 1999. The climate data of these two sites are summarised in Table 4.

On each monument, the test sets were placed on top of the north tower, exposed to rain. The stone cubes were inclined of 6°, facing south.

During the exposure of the limestone samples, samples of rainwater were collected every week, and the mix of the four samples was analysed monthly by a specialised laboratory. The average of the pH and the ions concentration during the six years exposure are presented in Table 5. According to the analyses, the rainfall is more acid in Langres than in Reims. But in Reims, the rainfall water contains more ions, especially chlorides, sulfates, sodium and calcium.

Table 4: Climatic data of the exposure sites

Sites	Reims	Langres
Altitude of the city (m)	83.0	466.0
Height of the north tower (m)	80.0	25.0
Monthly average of highest temperature (°C)	16.0	15.1
Monthly average of low temperature (°C)	1.3	-1.0
Annual mean temperature (°C)	11.4	10.2
Annual rainfall (mm)	591.0	877.0
Frost zone	Moderate	Severe

Table 5: Water rainfall analyses carried out on weekly samples: average values over the 6.5 years.

Sites	pH	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Reims	6.6 ±0.7	3.0 ±1.8	1.1 ±0.8	1.5 ±0.5	1.2 ±0.9	1.7 ±1.1	0.5 ±0.4	0.2 ±0.1	3.8 ±1.8
Langres	5.9 ±0.7	1.3 ±0.7	1.2 ±0.9	0.8 ±0.4	0.8 ±0.7	0.7 ±0.5	0.4 ±0.4	0.2 ±0.1	2.0 ±1.0

After 20 months of exposure, the sets were brought back to the laboratory, put in a conditioning chamber (58% RH and 20°C) before the mass and colour measurements were made. Two months later, they were re-installed on the respective sites.

Finally, after six years and a half, the sets of samples were definitely removed from the sites.

3 Results

3.1 Mass evolution

After six and a half years of exposure, only small variations of mass were observed, except for the Champagne chalk and the Charentenay stone, which sometimes broke into pieces. There was no visible difference in the mass loss between treated and untreated samples (Table 6). For all lithotypes, the weight loss for samples exposed in Langres was higher than for those exposed in Reims.

Table 6: Mass change after exposure (%).

Treatments	Sites	CO	SA	CR	CH	JA	LA
Untreated	Langres	-0.24	-0.25	**Broken**	-0.14	-0.32	-0.39
	Reims	-0.17	-0.22	-0.36	-0.18	-0.18	-0.19
Imlar	Langres	-0.33	-0.04	**Broken**	-0.20	-0.02	-0.15
	Reims	-0.16	0.01	-0.25	-0.06	-0.01	-0.06
H224	Langres	-0.04	-0.24	-0.13	**Broken**	-0.20	-0.24
	Reims	-0.08	-0.19	-0.21	-0.08	-0.17	-0.13
DF104	Langres	-0.13	-0.28	**Broken**	**Broken**	-0.26	-0.25
	Reims	-0.14	-0.21	**Broken**	-0.07	-0.18	-0.14
VP1311	Langres	-0.07	-0.25	-0.42	-0.18	-0.21	-0.27
	Reims	-0.04	-0.16	-0.84	-0.21	-0.22	-0.20

3.2 Colour changes

For most limestones, the colour variations were largely due to a change in lightness. Thus, only the evolution of the difference of lightness as a function of the time of exposure is considered hereafter. The example of Courville stone is displayed for both sites, Reims and Langres (Figure 3), as the changes were similar for all stone types.

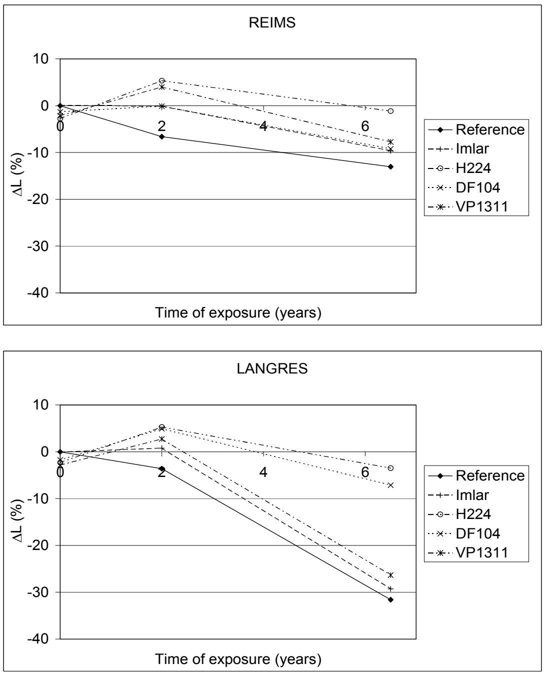

Figure 3: Difference of lightness as a function of the time of exposure. Example of Courville stone.

A decrease in the lightness difference over the years is observed for the untreated (reference) samples.

However, treated samples tend to show first an increase and then a decrease in this parameter. Thus these samples lighten during the first two years of exposure and darken subsequently.

After 6.5 years of exposure, the darkening is more pronounced in Langres than in Reims.

3.3 Contact angle

After exposure, most of the contact angles are lower than 60°, corresponding to class 1 and 2 (Table 7). Only stone samples treated with H224 still present a hydrophobic surface on the chalk stone and the Charentenay stone, with a contact angle belonging to class 5.

Table 7: Contact angle classes, after exposure.

Treatments	Sites	CO	SA	CR	CH	JA	LA
Imlar	Langres	1	1	**Broken**	3	2	2
	Reims	2	2	2	2	2	2
H224	Langres	2	1	5	**Broken**	2	2
	Reims	3	2	5	5	1	2
DF104	Langres	2	1	**Broken**	**Broken**	1	1
	Reims	2	1	**Broken**	2	1	1
VP1311	Langres	1	1	1	1	1	1
	Reims	1	2	2	1	1	1

3.4 Capillary water absorption measurements

After exposure, the Imlar surface film showed numerous lacunas. As the water can penetrate the stone through these lacunas, water absorption measurements were not considered valid. Thus the samples treated with Imlar were not tested.

Capillary water absorption coefficients (W), of the Courville, Savonnières and Jaumont stones, characterised by low capillarity, after six years of exposure, are presented in Figure 4. It can be seen that the micro-emulsion, VP1311, is no longer efficient after exposure. The water absorption coefficients of the treated and untreated samples are similar, regardless of the stone type. For the case of the H224 and DF104 products, the loss of hydrophobicity is more important on the samples exposed in Langres than for those exposed in Reims.

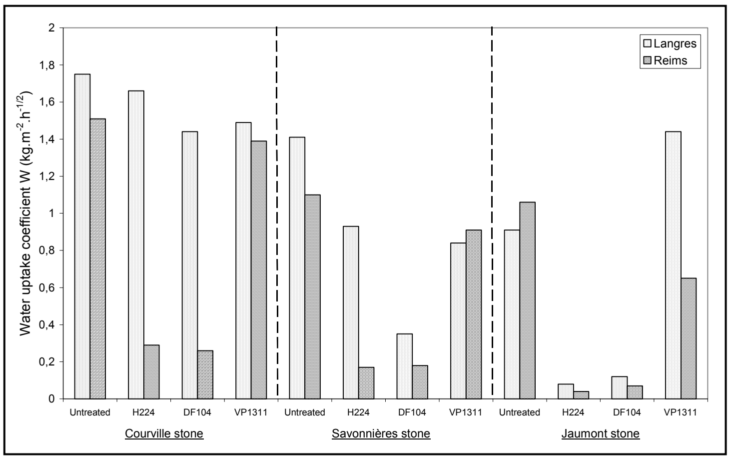

Figure 4: Capillary water absorption coefficients (W) for Courville, Savonnières and Jaumont stones after exposure at the two sites.

The behaviour of the Champagne chalk and the Charentenay stone, having high capillary, is different. The water absorption coefficients for these samples are shown in Figure 5. The samples treated with H224 or DF104 either broke into pieces during the first winter of exposure or present a very good efficacy. Their water absorption was still very low, with W values under 0.1 kg.m^{-2}.h$^{-1/2}$, represented by a black triangle on Figure 5. On the contrary, none of the samples treated with VP1311 broke and still showed some reduction in their capillary water absorption.

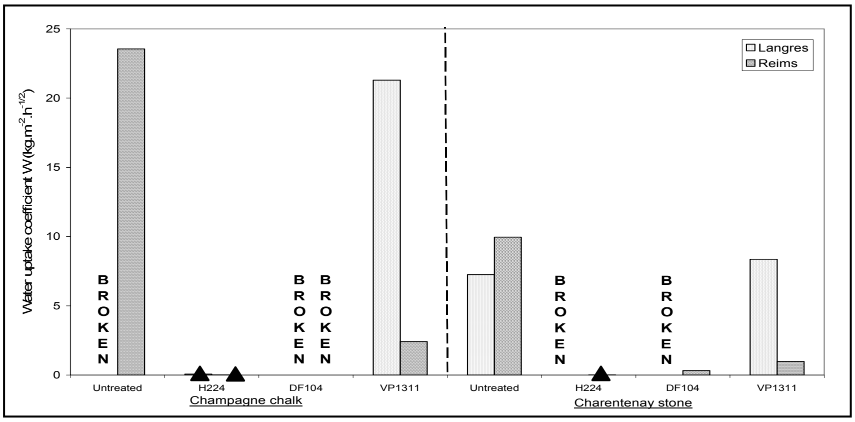

Figure 5: Capillary water absorption coefficients (W) for Champagne chalk and Charentenay stone after exposure at the two sites.

In Figure 6, these same water absorption coefficients are displayed as a function of the penetration depth of the water repellent products. Three groups are identified. First of all, the samples with a good water repellent penetration (between 4 and 10 mm) have a very low water absorption coefficient (lower than 0.1 kg.m^{-2}.h$^{-1/2}$). All of the samples from this first group had been treated with H224.

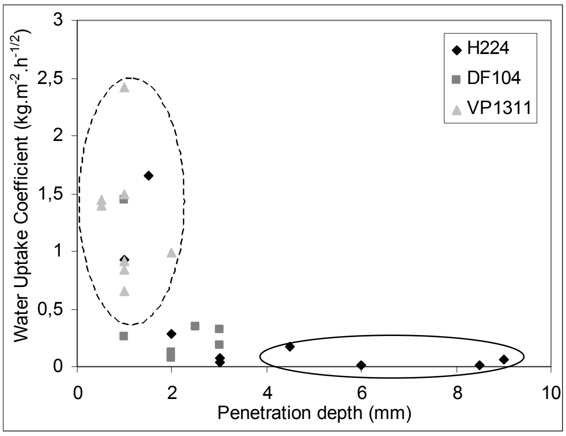

Figure 6: Capillary water absorption coefficient (W) for the Champagne chalk and the Charentenay stone after exposure as a function of the depth of penetration of the applied products.

The second group corresponds to those samples with a poor water repellent penetration depth, i.e. lower than 2 mm. After 6.5 years exposure, their W values vary from 0.7 to 21.3 kg.m^{-2}.h$^{-1/2}$. These are mostly samples treated with VP1311.

The last group of samples is formed mostly by those treated with DF104 and H224. These had a medium penetration depth, ranging from 1 to 3 mm, and their W values after exposure were found to be between 0.0 and 0.4 kg.m^{-2} h$^{-1/2}$.

4 Discussion

The behaviour of the samples treated with the various water repellent products show a noticeable difference between the two exposure sites. In fact, the mass loss, which is a consequence of surface dissolution, and the surface darkening are stronger on samples exposed in Langres than on samples exposed in Reims. The dissolution can be directly related to the climatic conditions, which are more severe in Langres (higher annual rainfall, lower temperature with numerous days of frost, lower pH of the rainwater, etc.).

The results of contact angle measurements show that, after ageing, there is little water repellency left on the surface of the samples (Table 7), as a result of the probable deterioration of the water repellent at the surface, during the surface dissolution process of the limestones. However, this phenomenon is only superficial. In fact, the water uptake coefficients are still very low for samples with good water repellent penetration depth (Figure 6), proving that the product is still effective within the stone. This confirms the observations made by Bruchertseifer [10] after artificial ageing of stone samples and by Puterman [11] on mortar samples.

Some of the water repellent treatments, i.e. Imlar and VP1311 show poor effectiveness and durability, while others, such as H224 and DF104, both show good results. The film-forming acrylic resin Imlar, containing Teflon, leaves lacunas open in the film that covers the stone. Thus the surface is heterogeneous and not acceptable from an aesthetic point of view apart from the fact that water can penetrate into the stone through these lacunas. The micro-emulsion VP1311 showed poor durability on the stones tested in this study, mostly as a result of its poor penetration depth. However, De Witte [6] observed on different building materials, such as Euville, Massangis and Savonnières stones and bricks, that after artificial ageing, the effectiveness of water repellent mixtures based on water emulsions is similar to the one of water repellents dissolved in organic solvents. Thus it shows that the durability of a treatment strongly depends on the stone properties and the weathering conditions.

Finally, DF104 and especially H224 are efficient and durable on most stones, except Courville stone, because its very fine pore structure cannot be penetrated by these water repellent products. After few years of exposure, the water repellent, which is only at the surface of the stone, is not efficient anymore. Moreover, these two treatments, when applied to very porous stones such as chalk and Charentenay limestones, that show a high capillary absorption and susceptible to frost damage, can lead to serious damage when exposed to frost.

5 Conclusion

Of the tested water repellents based on silicon, those dissolved in solvent, showed the best durability. However, on a long-term basis, they cannot protect effectively limestones which have very fine pores.

Determining whether a product shows a good durability is one thing, trying to find which of the three groups of factors, i.e. stone properties, climate or atmospheric pollution, is the most important, is rather difficult in our case. Further experiments should be performed on a larger scale in order to get more contrasted climate conditions, or similar pollution levels in a same climate. We could at least confirm, based on our results, that pore size distribution and thus intrinsic stone properties are a key factor concerning treatments' durability.

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