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# Water-repellent and biocide treatments: Assessment of the potential combinations

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## Abstract:

It is a common practice to use several chemical products during restoration projects of monuments or sculptures. However, care must be taken when combining the products to avoid a misuse. For example, it is well-known that applying a biocide on stone before a water-repellent leads to a diminishment of the hydrophobic effect of the treatment. But the application of biocide after a water-repellent treatment has been poorly analysed, although studies have proven that the stone loses its hydrophobicity after the application of the biocide. Henceforth, this study investigates the effects of biocide application on a water-repellent film and focuses on the possibilities to restore the efficiency of the previous water-repellent treatment (after the application of the biocide). At first, the tests were performed on glass slides to understand the mechanisms, with the subsequent results revealing that the biocide product deposits on the water-repellent film. Then, the study focuses on determining methods to remove the remains of biocide on limestone samples, previously treated with a water-repellent. The water-repellent used in the study is an alkylpolysiloxane, Rhodorsil H224 from Rhodia.

**Keywords:** Water-repellence; H224; Biocide; Limestone; Microdrop test.

## 1. Research aims

A scientific research was carried out to evaluate the modifications induced by the application of a biocide based on quaternary ammonium on hydrophobic stones, previously treated with the water-repellent H224. The study deals with the assessment of the effects of biocide application on a water-repellent film and with the investigations of the possibilities to restore the hydrophobicity.

## 2. Introduction

The key function of a water-repellent is to prevent liquid water penetrating into the masonry, by capillary action [1]. The subsequent surface modification should reduce the microbiological colonisation, due to the limited access of moisture. However, the water-repellents do not prevent the growth of microorganisms, but simply delay it. As a matter of fact, microbial contamination of treated rock surfaces has been observed in long-term studies of exposed treated stones [2, 3]. Thus biocide treatments might be required on treated stones after years of exposure. Although biocide products are usually applied to destroy microorganisms on monuments, more and more are used to prevent any further re-colonisation. Nowadays, in some European countries, researchers recommend to apply

a protective treatment and a biocide at the end of restoration works to waterproof the stone and inhibit re-colonisation for long periods [4].

Nonetheless, combining several treatments must be executed with care as the products can interact with each other causing negative effects [5]. For example, the importance of waiting after the application of a biocide before treating with a water-repellent is now well-known amongst restorers. Indeed laboratory studies have shown that biocides may hinder the polymerisation of water-repellents [6, 7]. But the case of the application of biocide after a water-repellent treatment has been approached scarcely, concluding that no apparent problem appears [6]. The French institution, CEBTP, and the firm Rhone-Poulenc found evidence that biocide treatments, based on quaternary ammonium salts, disrupt the hydrophobic effect of former water-repellent treatments, such as polysiloxanes [7, 8]. In this investigation, performed in 1985, biocides were used to eliminate the green biocolonisation on full scale models of stonewalls, which were treated with several water-repellents 15 years before. Before any treatment, the water-repellency, evaluated by in situ water uptake measurements, was between 90 and 100% of the initial one [7]. After the biocide treatment, the full scale models were then retreated with Rhodorsil H224. This treatment did not perform well, as revealed evaluated by in situ water uptake measurements, which increased significantly (around 20%, with respect to the value measured after 15 years of ageing, before any treatment). On the basis of these results, a laboratory research was performed by the same institutions to quantify the water uptake of stone samples after each one of the four following consecutive treatments: (i) water-repellent application; (ii) biocide application; (iii) water rinsing; and (iv) water-repellent application. The study [8] confirmed that there was no remaining hydrophobic effect after the application of biocide, but also proved that in fact, the hydrophobic effect can be partially or entirely re-established, according to the nature of the products used, after rinsing with water. This study contradicts the thought that a biocide treatment does not interact with a previous water-repellent treatment.

Besides, in the field, where biocides are used to eliminate microorganisms, Nugari and Salvadori [5] noticed that conservators generally remove the biocide product, after its action has taken place. This is usually done by washing the surface with water, during the surface cleaning phase of the restoration plan. Also, Lazzarini and Laurenzi Tabasso recommend that biocide treatments “should always be followed by abundant rinsing in order to remove any residues of the biocide” [9]. However, even on a hydrophobic surface, water rinsing is not advised for sculptures, ornaments or weak masonry. Can poultices, that are commonly used to remove salts on stone masonry, be applied to remove remains of biocide after a treatment? Is the hydrophobic effect of the water-repellent treatment entirely restored? These are the issues that will be discussed in the following study, focusing on biocides based on quaternary ammonium salts, as they are more environmental-friendly products. (A directive from the European Community limits the use of organic compounds, and thus the emulsion in water solvent is to be preferred.)

Table 1  
Petrophysic properties of Courville and Saint-Maximin stones

	Density	Water porosity (%)	Mercury porosity (%)	Mean pore diameter ( $\mu\text{m}$ )	Capillary water absorption ( $\text{kg m}^{-2} \text{h}^{-1/2}$ )
Courville	2.2	17.8	21.9	0.16	1.5
Saint-Maximin	1.7	35.3	33.7	13.21	16.1

### 3. Materials and methods

#### 3.1. Materials

Two different French limestones are selected for the study, because of their different petrophysic properties. The first stone, from Courville, is dense with fine pores and it has a low capillary water absorption while the Saint-Maximin stone is macroporous and has a high capillary water absorption (Table 1). The Courville stone is cut in cubes with edges of 50 mm and the size of the Saint-Maximin stone samples is 50 x 50 x 80 mm. There are four samples of each limestone. To allow a better understanding of the phenomena, some of the tests are also performed on glass slides before testing the limestones. Indeed, the glass slides have a flat and non-porous surface, thus the problems of roughness and porosity are avoided. The 15 glass slides are those commonly used for thin sections (size 30 x 45 x 1.6 mm).

#### 3.2. Experimental set-up

##### 3.2.1. Water-repellent treatment

First of all, the samples are treated with a water-repellent, an alkylpolysiloxane: Rhodorsil H224 from Rhodia. The mixture, of 10% H224 in white-spirit, is applied on all the glass slides by dip-coating, while the stone cubes are treated by brush until no more product is absorbed by the stone. The water-repellent is applied only once, on the top surface of the stone samples. The samples cure during 28 days at 20°C, 58% of relative humidity (RH), following recommendations established according to our previous studies. Once the product is cured, the “dry matter” is determined on the limestone samples. The dry matter ( $d$  [g m<sup>-2</sup>]) evaluates the amount of active product that remains in the stone after treatment:

$$d = \frac{m_c - m_o}{S}$$

$S$ : treated surface of the sample [m<sup>2</sup>];  
 $m_o$ : mass of the sample before treatment [g];  
 $m_c$ : mass of the sample after curing [g].

The dry matter in the Saint-Maximin stone is almost three times the one in Courville limestone (Table 2).

Table 2  
 Dry matter and penetration depth in the stone cubes after water-repellent treatment

Stone	Dry matter (g/m <sup>2</sup> )		Penetration depth (mm)	
	Mean	Min–Max	Mean	Min–Max
Courville	557	435–732	4	2–7
Saint-Maximin	1411	1275–1543	8	6–10

##### 3.2.2. Biocide treatment

After curing, the samples are treated, by brush, with a ready-to-use biocide, of quaternary ammonium type: Proxymousse (benzododecinium chloride, concentration < 2.5%, as indicated in the technical

data sheet). The treatment is repeated three times, with 1 day interval between each application. All glass slides are treated in the same way, except three of them that remain as references. The samples stand for 28 days at 20 °C and 58% RH, before any measurement.

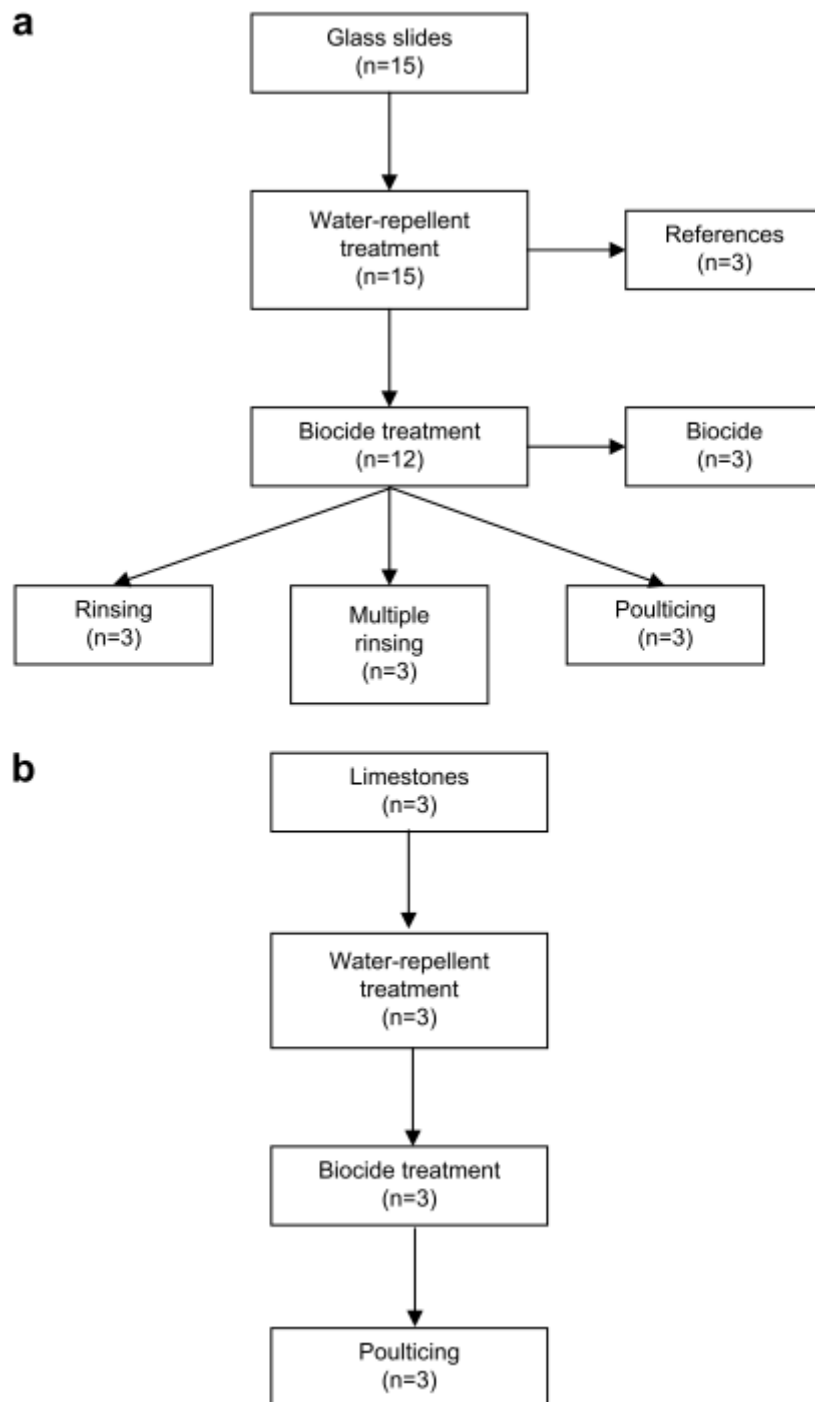


Fig. 1. Experimental set-up for glass slides (a) and for limestone (b).

### 3.2.3. Elimination of the biocide

To eliminate the remains of biocide on the water-repellent film, three different methods are tested, on three glass slides each time (Fig. 1a): - rinsing with distilled water, by spray; - rinsing with distilled

water, by spray, repeated three times; - application of poultices made of cellulose powder and distilled water.

While the first two techniques are modified from the CEBTP experiment [8], the last one is adapted from the common use of poultices to remove salts from a stone. According to the results obtained on the glass slides, only the more efficient method is tested on the stone cubes (Fig. 1b).

### 3.3. Tests

For the analyses, the reference is the sample treated with the water-repellent and not the raw glass slide or stone.

#### 3.3.1. Optical microscope observations

The glass slides are studied under an optical microscope Leica DMRM, by transmission. The magnification is first 10 and then 400.

#### 3.3.2. Microdrop absorption (according to RILEM Test n°II.8b) [10]

Microdrop absorption is used to assess the water-repellence of the outermost zone. The rate of a microdrop absorption by capillary action decreases in treated stone, due to the hydrophobic effect of the water-repellent film formed on pore walls. A drop of 5 mL is deposited on the surface of the stone. The time necessary for its complete absorption or evaporation is registered. At first, the test of the microdrop is performed on the glass slides, then on stone samples. On glass slides, there is no water absorption, only evaporation of the drop occurs, because there is no porosity. On stone samples, both phenomena, absorption and evaporation, can occur at the same time.

During the testing, four drops are applied on each glass slide, while nine drops are applied on the stone surface.

#### 3.3.3. Determination of water absorption coefficient by capillarity (European standard EN1925) [11]

This test is useful for assessing the success of a water-repellent treatment. 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 is put in contact with water. The stone samples are weighed at regular intervals, during 48 h. The water uptake coefficient  $W$  [ $\text{kg m}^{-2} \text{h}^{-1/2}$ ] represents the amount of water absorbed per square metre as a function of square root of time. This test is repeated three times on each sample: after application of the water-repellent treatment (the reference), after application of the biocide treatment and after poulticing.

#### 3.3.4. Penetration depth measurements

At the end of the experiments, the limestone cubes are cut in two pieces, then soaked in water and the penetration depth is measured on the freshly cut surface as the borderline of “wetness” is clearly visible.

## 4. Results

### 4.1. Glass slides

#### 4.1.1. Optical microscope observations

On Fig. 2, two images are depicted, Fig. 2a showing the glass slide coated with water-repellent, and Fig. 2b, the same glass slide after application of the biocide. In Fig. 2a, the water-repellent film appears to coat the glass slide uniformly, except for some small defects (bubbles, dust . . .). Fig. 2b reveals that the water-repellent film, which is uniform, is covered with areas of irregular shapes, delimited by a darker edge, which most probably correspond to remains of the biocide. The whiter spots look like a crystallisation of an undefined product.

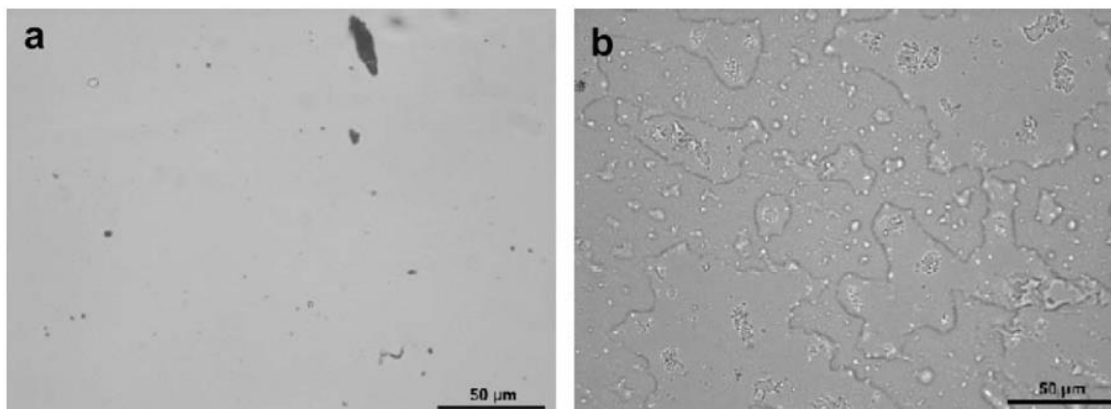


Fig. 2. Microscope pictures of the glass slide. (a) Water-repellent film, and (b) water-repellent followed by biocide treatment.

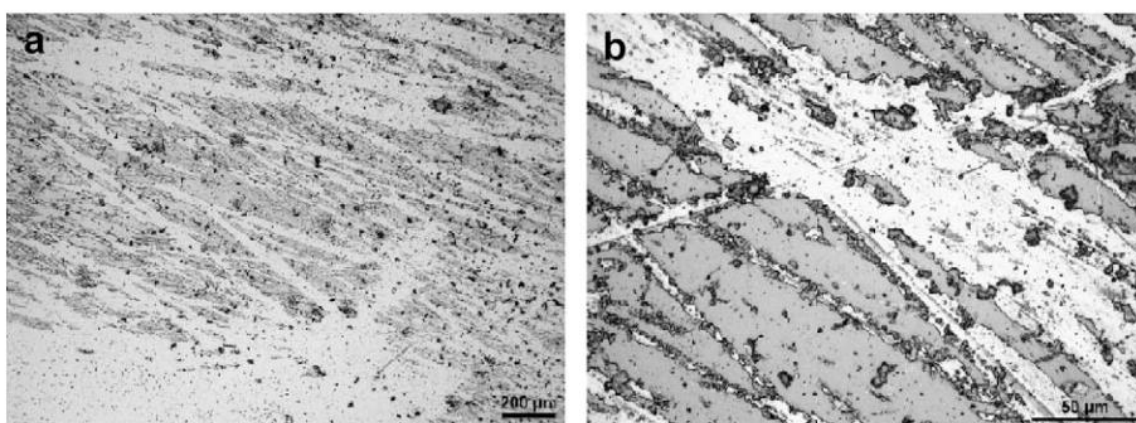


Fig. 3. Microscope pictures of the glass slides after the following treatments: water-repellent/biocide/water rinsing. (a) General view, and (b) detail.

After spraying water, the surface of the glass slide appears very inhomogeneous, as shown in Fig. 3. In Fig. 3a, there is a juxtaposition of grey zones and white stripes, which have different orientations. The grey zones are assumed to be remains of the biocide product, while the white stripes correspond to the water-repellent film. At higher magnification, in Fig. 3b, the edges of the remains of biocide are put in evidence: they are neat and indented, clearly separated by the white stripes of the water-repellent film. This heterogeneous distribution of the biocide remains is probably due to the application technique with the brush, which creates more or less thick stripes of a biocide product.

By spraying water, the less thick areas of biocide are cleared preferentially. When repeated several times, the rinsing allows for a slightly better cleaning of the surface: less residues of biocide are visible on the water-repellent film, but the surface is still not evenly cleaned. To conclude, it is obvious that

the water spraying is not satisfactory. The cleaning is not homogeneous, as the biocide product is only partially removed from the surface of the water-repellent film.

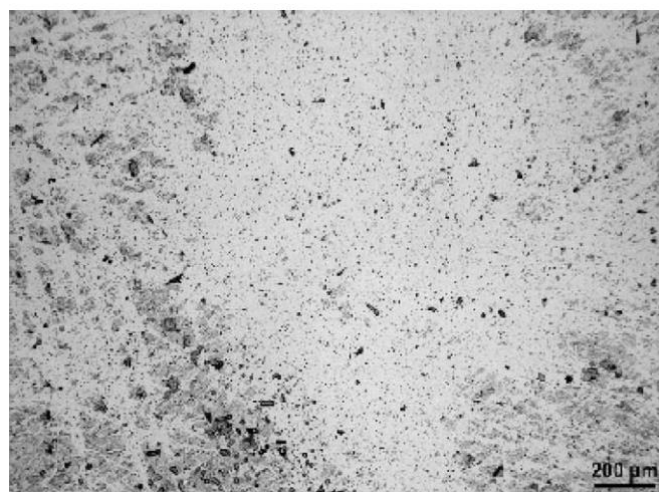


Fig. 4. Microscope picture of a glass slide. After cleaning with poultices.

Looking at Fig. 4, the application of poultices leads to a better elimination of the biocide product on the surface, than the technique of water spraying. Only some small darker zones (biocide product remains) are visible, while most of the surface corresponds to the water-repellent film in light grey. However, some residues of the poultice (black particles) are clearly noticeable on the surface.

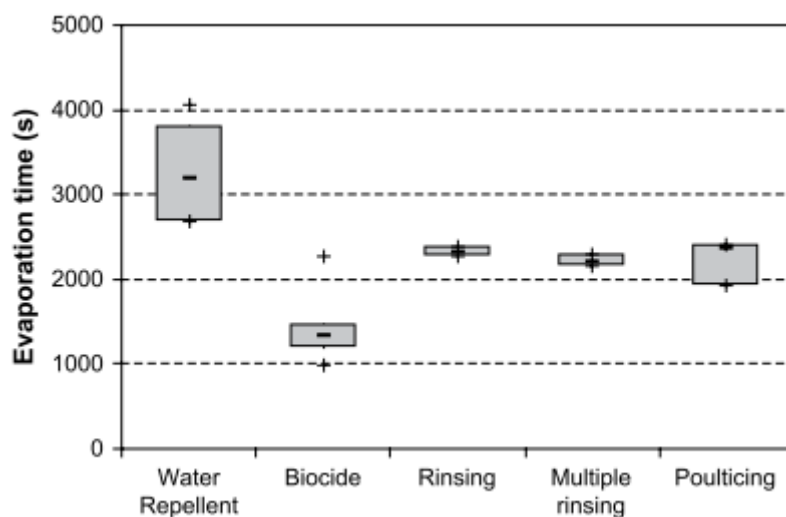


Fig. 5. Results of the microdrop test on the glass slides.

#### 4.1.2. Microdrop absorption

The results of the microdrop test on the glass slides are displayed in Fig. 5. The evaporation times for the reference samples, i.e. the evaporation time on samples treated with a water-repellent, are widespread, between 2 679 and 4 057 s. Within the frame of this study, the mean value, which is over 3 000 s, will stand as a reference of a good water-repellent treatment. After the application of the biocide, the evaporation time drops considerably. The mean value is only 43% of the reference evaporation time, but the values are still widespread. Single and multiple rinsing allow for a same



increase of the evaporation time, reaching 71% of the water-repellent reference value. The repeated rinsing on glass slides does not increase the evaporation time. Moreover, the range of evaporation times, after rinsing, is now very narrow. The values of evaporation time after poulticing are less homogeneous, but the mean value is almost the same, reaching 69% of the reference value.

The different techniques used to remove the biocide lead to an increase of the evaporation time. Nonetheless the value is still lower than the reference time (water-repellent treatment).

## 4.2. Stone cubes

### 4.2.1. Penetration depth

The penetration depth of the H224 is lower in the Courville stone (4 mm) than in the Saint-Maximin stone (8 mm) (Table 2).

### 4.2.2. Microdrop absorption

For the two types of limestones, the reference value, i.e. the evaporation time on samples treated with a water-repellent, is slightly different, but in the same range: over 3 000 s, as shown on Fig. 6. After the application of the biocide, a high decrease of the evaporation time is observed: there is a drop of 90% for the Courville stone, while the evaporation time for the Saint-Maximin stone falls down to 10 s. After poulticing, the level of the evaporation time is restored at 80% of the reference value for the Courville stone and even 99%, in case of the Saint-Maximin stone. The poultice is a very efficient way to bring back the level of evaporation time close to its reference value, after the drop down due to the application of a biocide treatment.

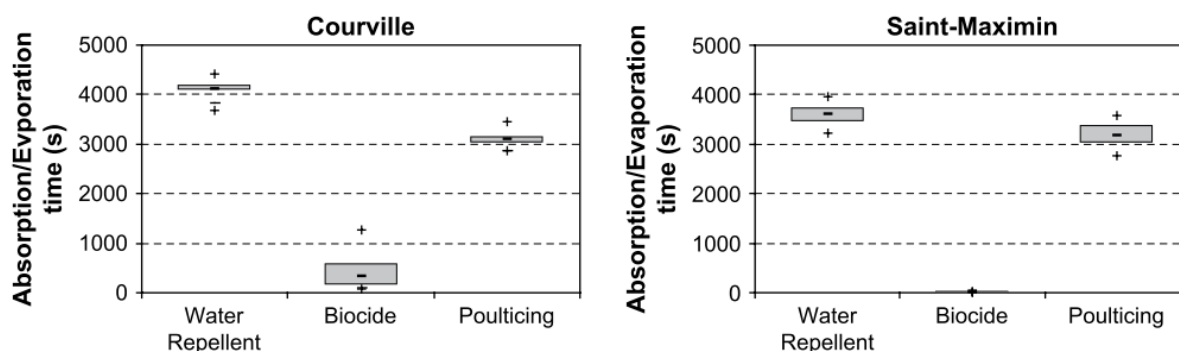


Fig. 6. Results of the microdrop test on Courville and Saint-Maximin stones.

### 4.2.3. Water absorption by capillarity

After the microdrop test, the water uptake coefficients are measured on the limestone samples. The results are displayed in Table 3. After the water-repellent treatment, the absorption is very low: on both stones, the coefficient is under  $0.1 \text{ kg m}^{-2} \text{ h}^{-1/2}$ , which is the reference value for a good water-repellent treatment in the literature [12]. After the biocide treatment, the water uptake coefficient raises. The increase is more noticeable on the Saint-Maximin stone, since it is more porous and capillary than the Courville stone, as shown in Table 1. After poulticing, the water uptake coefficient is

brought back to the reference level of  $0.1 \text{ kg m}^{-2} \text{ h}^{-1/2}$ . The study of the water absorption by capillarity test charts (Figs. 7 and 8) can give a clearer indication about the capillary behaviour of the stone samples. The curve of the sample treated with the water-repellent is almost linear with a low slope. The water-repellent film prevents water to penetrate the stones pore system. After the biocide treatment, there is a great increase of the water uptake of the Saint-Maximin stone at the very beginning (the first 10 min), proving that water penetrates the pore system of the stone.

Table 3

Water absorption coefficient for Courville and Saint-Maximin stones ( $W$  in  $\text{kg m}^{-2} \text{ h}^{-1/2}$ )

$W$ ( $\text{kg m}^{-2} \text{ h}^{-1/2}$ )	Water-repellent	Biocide	Poulticing
Courville	0.06	0.21	0.10
Saint-Maximin	0.04	3.09	0.12

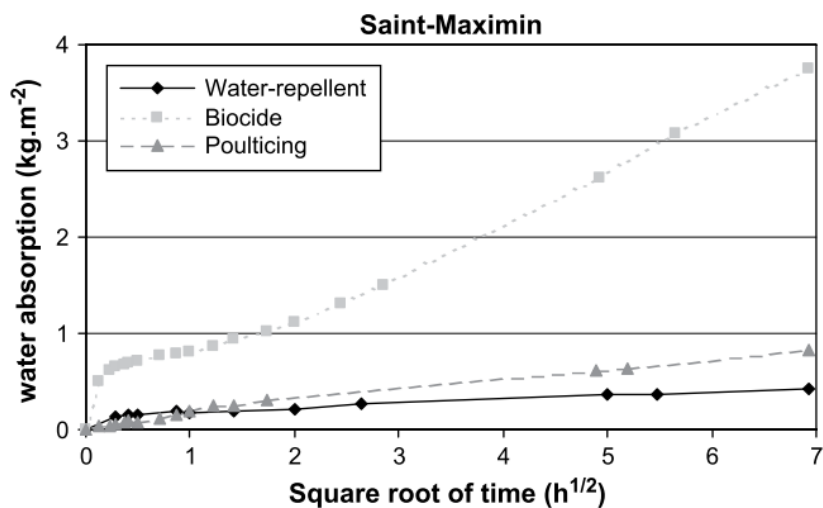


Fig. 7. Water absorption capillarity charts for Saint-Maximin stone.

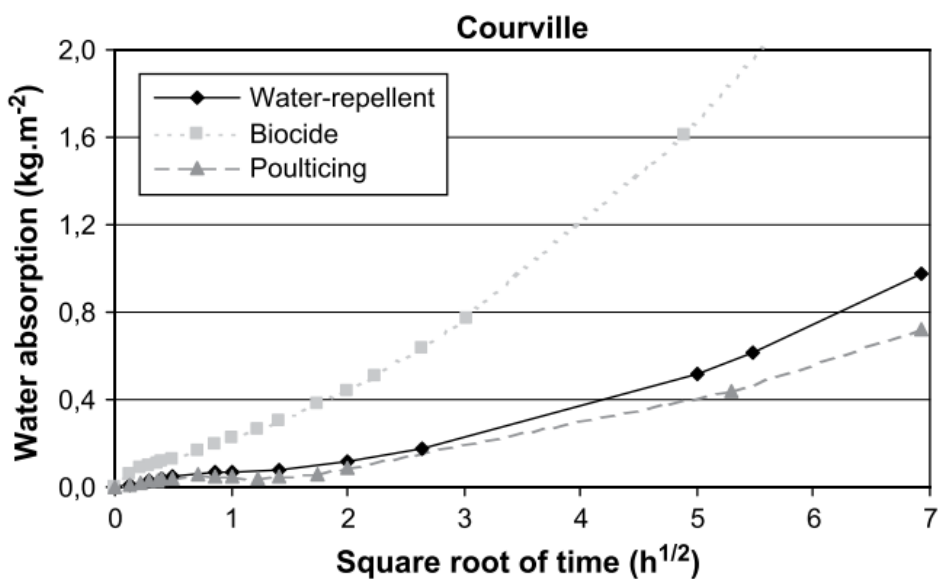


Fig. 8. Water absorption capillarity charts for Courville stone.

Then a decrease of the slope is observed: after penetrating few millimetres of the pore system, the water seems to be prevented from any further penetration. However, after 1 h, another slower increase starts: the water is reaching the rest of the pore system. Because of the lower water uptake coefficient of the untreated stone, the phenomena are less visible on Courville limestone (Fig. 8) but still occurs.

The “poulticing” curve is almost a straight line, following the reference curve. At the beginning, the slope is slightly lower than the reference one, while after 1 h, it is higher. The absorption behaviour of these two samples is very similar: it is very hard for the water to penetrate into the capillary system of the stones.

## 5. Discussion

Thanks to the study on the glass slides, it is underlined that the biocide treatment leaves a non-homogeneous layer, on the surface of the treated samples, which modifies the hydrophobic properties of the material. Indeed, the biocide product contains quaternary ammonium salts, which act as surfactants, and so reduce the surface tension of the material. After the application of the biocide, on some parts of the water-repellent film, where the product remains, water drops spread on the surface, and the evaporation time is therefore reduced. The same phenomenon occurs on the stone surface as well. The water-repellent that deposited in the first millimetres of the stone acts as a barrier against water, and thus the evaporation time of a drop on the stone surface increases, while the water uptake coefficient decreases significantly. When a biocide is applied on a stone previously treated with a water-repellent, the biocide treatment is deposited in the first millimetres inducing a good wettability of the stone when put in contact with water. The biocide application clearly reduces the surface hydrophobicity of treated stones, and modifies their capillary behaviour. In that case, it is very important to have a higher penetration of the water-repellent than the one of the biocide treatment. Thus, if the water-repellent penetrates far enough in the stone, there is still an action from the water-repellent, preventing penetration of water further inside the stone.

Therefore, if, for a study, measurement of the hydrophobic properties is required on stone colonised by microorganisms, it is possible to treat the stone with biocide, to remove the remains of product by poulticing and finally to make the measurements without any modification due to the biocide treatment. However, by poulticing the treated surface, persistence of the biocidal effect is lost immediately; on the other hand the biocidal effect of quaternary ammonium salts does not keep on for a long time, as the product can be rapidly dissolved in rainwater. Biocides based on quaternary ammonium salts can be used to remove an existing layer of biocolonisation on water-repellent surfaces but it can not be used to maintain biocidal effects combined with water-repellent treatments for long period as it hinders the hydrophobic effects.

Attempts to combine water-repellent and biocide treatments have been made to maintain biocidal effect for long periods, using other chemical types of biocide. The application of a mixture containing both the biocide and water-repellent products appears to show good performance to control growth of microorganisms [4], which was studied carefully but the water-repellency of the treated surface was neither tested after treatment nor after exposure. It is thus difficult to know if these authors faced the same kind of problem as the one reported in our study. It is important to stress that both biocide and water-repellent treatments should be tested separately but also in combination

on samples, before any application on monuments surfaces, as their action can be modified by mixing. Moreover, biocidal properties and water-repellent efficiency should be tested to check the effectiveness of the different products used.

## 6. Conclusion

It is now proven that, whether a biocide is applied before or after a water-repellent treatment, negatives effects are observed. In the field of conservation, it was already well-known that a water-repellent is not efficient if applied on a surface previously treated with a quaternary ammonium biocide. The present study establishes that there is also a loss of hydrophobicity when the application order of the treatments is inverted, i.e. when biocide is applied after the substrate has been treated with the water-repellent.

Our results put in evidence that the biocide is restricted to a superficial layer of the substrate, treated with a water-repellent. Thus, the hydrophobic property diminishes near the stone surface and not in depth. Moreover, the investigation reveals that the remains of biocide product near the stone surface can be easily removed by poulticing, while water rinsing is not recommended. This tends to prove that the biocide product is only deposited on the surface of the water-repellent film, apparently where no chemical interaction occurs. Indeed, in case of a loss of water-repellence due to biocide application on a substrate, the previous hydrophobicity will be recovered almost entirely after poulticing.

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