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Tests of two Water Repellent Substances on Brick: do they delay the Regrowth of Biofilms? The Case of the Cathedral of La Plata, Buenos Aires Province, Argentina

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Abstract

This is a study about the Cathedral of La Plata (Buenos Aires Province, Argentina), a neogothic temple made out of brick masonry and mortar. The construction was started in 1884, and was opened as a chapel in 1902, but only started functioning as a Cathedral in 1932. Then, the towers and many ornamental details were completed in 1999. As these works were in progress, the building was cleaned and a hydrophobe substance was used.

Currently, the Cathedral is affected by the growth of lichens, green algae, cyanobacteria, mosses, and higher plants, especially in the humid places looking to the South and South East, so new cleaning and protection works are being planned. There are two big aims: first, to find an adequate cleaning process that is effective against biofilms without harming the material; and second, a water repellent treatment that delays new growth of microorganisms as much as possible.

Although hydrophobe substances have no biocide effect, they block water absorption, so there is almost no water available for microorganisms. So, in theory, water repellents would have a double protective action: prevent the damage caused by water to materials create a barrier for biofilms, since microorganisms find it harder to grow on a surface with very low moisture.

Material studies were performed to determine their composition, specific weight and water absorption. The ancient bricks absorbed up to 23% of their dry weight in water, and retained moisture up to one week.

To assess the action of the hydrophobes, colonized concrete and brick surfaces were cleaned with different methods: hydrojet cleaning; sodium hypochlorite; hydrogen peroxide; neutral pH detergent; cleaning paste ("papeta") AB 57 with benzalconium chloride as biocide. After that, the surfaces were rinsed with abundant water to remove the rests of the substances used. Quantitative samplings were performed prior and after the cleaning to assess the efficacy of the biocides.

The clean surfaces were allowed to dry three days and divided in three: one part was left untreated, and the other two were impregnated with different commercially available hydrophobes.

Follow up visual inspections and quantitative sampling of microorganisms showed in the short term (3 months) that there is no growth in the treated surfaces whereas the untreated surfaces had low microbial counts. Longer term inspections will determine if this trend lasts.

Keywords: brick, La Plata Cathedral, Argentina, biofilms, microorganisms

1 Introduction

The Cathedral of La Plata (Buenos Aires Province, Argentina), is a neogothic building with a surface of 7000 m^2 made out of exposed brick masonry and mortar, that gives it a very special and distinctive appearance. A white cement mortar was used in pinnacles, vault supporting arcs and ornaments. Although it is placed in the centre of the city, in a dense traffic area, the Cathedral is surrounded by a garden that helps mitigate the effect of car pollution as well as the influence of pollutants from the Petrochemical complex outside the city, and provides shade and humidity,

The original project was designed by eng. P. Benoit, and architect E. Meyer drew the definitive project, inspired by the Cathedrals of Colony and Amiens (Fig. 1 and 2) and the construction was started in 1884. After many years of works, the chapel of "Nuestra Señora de los Dolores" (Our Lady in Pain) was opened in 1902, but only started functioning as a Cathedral in 1932. Later, the crypt, designed was completed in 1940. In 1941, the floors were covered with granite slabs and in 1947 the vitraux from France were placed in the windows. Then, the building remained unconcluded until the towers and many ornamental details were completed in 1999 [1]. As these works were in progress, the building was cleaned and a hydrophobe substance was used [2] [3].

Now, after ten years, the Cathedral is currently affected by the growth of lichens, green algae, cyanobacteria, mosses [4],and higher plants. Lichens, namely *Caloplaca austrocitrina* grow especially in the humid places looking to the South and South East [5], so new cleaning and protection works are being planned.

Figure 1: Cathedral of La Plata

Although hydrophobe substances have no biocide effect, they block water absorption, so there is almost no water available for microorganisms. In theory, water repellents would have a double protective action: prevent the damage caused by water to materials create a barrier for biofilms, since microorganisms find it harder to grow on a surface with very low moisture.

This work has two big aims: first, to find an adequate cleaning process that is effective against biofilms without harming the material; and second, a water repellent treatment to delay the growth of new microorganisms as much as possible. Here we show the first results of the ongoing project.

2 Materials and methods

2.1 Weather

According to the data of Instituto de Gemorfología y Suelos (Institute of Geomorphology and Soils) of La Plata National University, La Plata has a mean annual rainfall of 1040 mm (obtained from 100 years data). The rainiest month is March, with an average of 111 mm and the less rainy is June, with 63 mm in average. The seasonal distribution of rain is rather regular, although there is a decrease in winter (Table 1).

Table 1: Rainfall distribution during the year

Summer (December, January, February)	289 mm	27%
Autumn (March, April, March)	289 mm	27%
Winter (June, July, August)	196 mm	18,8%
Spring (September, October, November)	266 mm	25, 6%

As regards the last 10 years, total rainfalls ranged from 1496 mm in 201 to 711,15 mm in 2008. (Fig. 2 – the data of 2010 is the accumulated rainfall up to July).

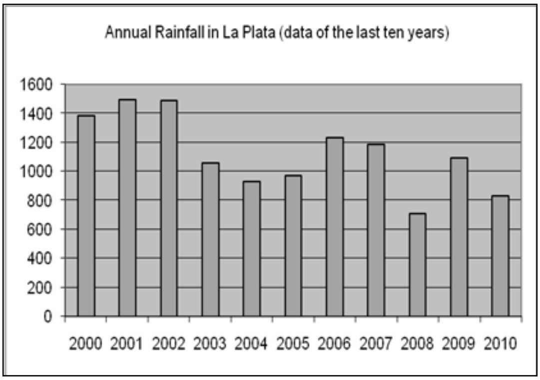

Figure 2: Rainfall 2000-2010

The mean annual temperature is 16.2 ºC. January is the warmest month with an average of 28 ºC and July is the coldest, with a mean temperature of 9.9 ºC. The extreme temperatures were 43 ºC and -5 ºC.

The mean annual wind intensity is 12 km/h, with a predominance of Eastern winds, and then NE and SW. The greatest intensities are observed during October, December and January, with averages of 7 to 15 km/h. It is important to note that winds from NE and NW carry with them industrial pollutants from the Petrochemical complex in the neighbor localities of Berisso and Ensenada.

The average relative humidity is 77%, varying between 85% in June and 70% in January.

Materials:

Brick samples were obtained from the wall with water cooled diamond-edge drill. Samples were 7.5 cm diameter and 25.0 cm deep.

Material studies were performed to determine their composition, water absorption and retention rates.

Natural humidity of the material at different depths was measured by drying the samples in the oven at 100º C and measuring the weight difference.

To measure the water absorption rates, the samples were left in the oven at 100º C until they reached constant weight, immersed in water during 24 h and then weighed again after thoroughly drying the surface. The difference of wet weight and dry weight is then calculated as a percentage of the initial weight.

In order to measure the water retention rates, immersed brick samples were allowed to absorb water until they reached a constant weight and exposed to two different environments, one with 60 ± 3 % relative humidity and 22 º C± 2 temperature (dry environment) and the other with de 95 % ± 3 relative humidity (wet environment) and a temperature of the same range.

The composition of the materials was analyzed by XRD (X-Ray Diffraction) with a Philips 3020 Goniometer with a PW 3710 controller, using Cu-Kα radiation, Ni filter and 40 kV-20 ma. Small samples were also observed under SEM (Scanning Electron Microscope) and EDS microanalysis (Electron Dispersive Spectroscopy) were performed.

2.2 Hydrophobes tests

To assess the action of the hydrophobes, colonized concrete and brick surfaces were cleaned with different methods: hydrojet cleaning; sodium hypochlorite; hydrogen peroxide; neutral pH detergent; cleaning paste ("papeta") AB 57 with benzalconium chloride as biocide. After that, the surfaces were rinsed with abundant water to remove the rests of the substances used. The tests were performed on the brick masonry wall besides the Chapel door on street 53 street and the treatments were identified as follows:

601: hydrojet washing

602: hydrojet washing and hydrophobe 1

603: hydrojet washing and hydrophobe 2

701: washing with 50% sodium hypochlorite

702: washing with 50% sodium hypochlorite and hydrophobe 1

703: washing with 50% sodium hypochlorite and hydrophobe 2

801: washing with neutral detergent and 50% sodium hypochlorite spray before rinsing

802: washing with neutral detergent and 50% sodium hypochlorite spray before rinsing,and hydrophobe 1

803: washing with neutral detergent and 50% sodium hypochlorite spray before rinsing, and hydrophobe 2

The clean surfaces were allowed to dry three days and divided in three: one part was left untreated, and the other two were impregnated with different commercially available hydrophobes

Solvent 1 is a water repelling protection for external walls with a base of siloxanes in organic solvents The density (at 20º) is 0,8 kg/lt ; the drying time is 1 h at 20ºc - 65% rh and the pH is 5/6 liquid. It acts as a water repelling impregnation that penetrates in-depth porose surfaces by capillarity through the pores.

Solvent 2 is a surface hydrophobe with silanes and siloxanes in solvent base. I has a density of density 0,8 kg/lt, the pH is 7/8 and the drying time is not specified. It acts by preventing rain water penetration of porose, not fisurated materials, allowing the surfaces to breathe freely.

So, the most important difference, besides the chemical composition, is that the first one has penetration power, whereas the second is only superficial.

In addition, two ancient bricks were thouroughly cleaned and impregnated with the hydrophobes to be tested, finally brought to the abside (the most humid and shady place) and exposed on the roof at 22 m level.

These bricks were periodically observed to assess if biofilms were growing on the surface.

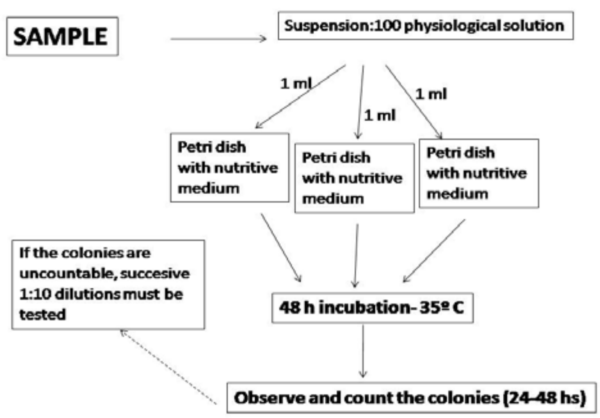

Figure 3: Scheme of the quantitative test

Quantitative samplings were performed prior and after the cleaning to assess the efficacy of the biocides, and then controlled again after a month and three months, in order to observe any regrowth. To identify the.organisms, the affected surfaces were gently scraped with a scalpel and the sample collected in sterile Petri dishes. The samples were then observed under microscope and the organisms were identified with the help of the pertaining bibliography. [6, 7, 8, 9, 10,11]

In order to assess the quantity of CFU (Colony Forming Units), a modification of the most probable number method was used (fig 3): a 10 x 10 cm square was carefully scraped, removing the biofilm that was carefully collected in sterile Petri dishes. Then, the samples were immediately labeled and brought to the laboratory.

The samples were placed in sterile containers and suspended in 100 ml of physiological solution. Warm agar- nutrient medium was poured in three sterile Petri dishes and allowed to cool. Before the agar became jellified, 1 ml of the suspension was poured in each Petri dish. The cultures are incubated at 35º C and the resulting colonies observed and counted at 24 and 48. In this case, no further dilutions were used, since preliminary tests proved that the number of colonies was adequate and the number of CFU could directly be estimated using the original suspension.

3 Results

3.1 Materials

The mean water absorption value obtained from three tests was 15.6%; the density in saturated state with dry surface is 1.7. The material´s porosity has as mean value of 23.6 %, determined as the quotient of the volume of water absorbed after 24 h and the volume of the sample.

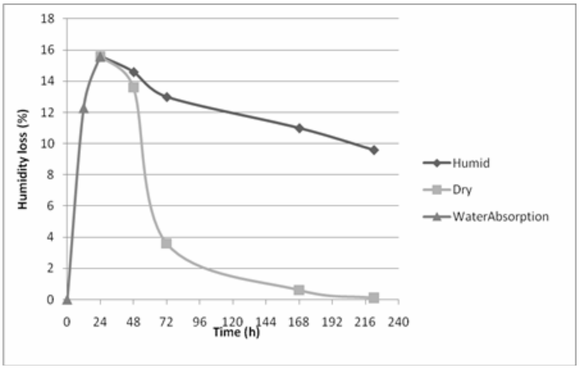

Figure 4: Humidity loss in dry and humid environment

When the brick's natural humidity was measured at different depths by weight loss at 100 Cº, the results showed that the sample with contact to the outside had less humidity than the inner one.

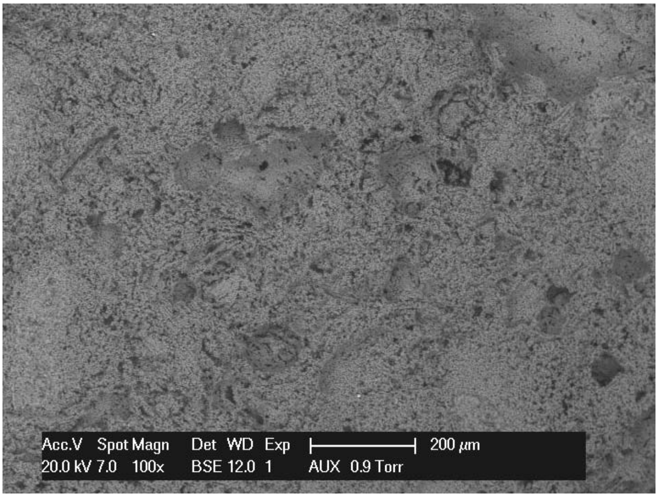

Figure 5: SEM Image

As regards the brick's water retention capacity, fig. 4 indicates the percentages of humidity retained by the samples related to time and environmental conditions. As it can be observed, there is a great influence of the environment's relative humidity percentage in the material's water retention, creating a suitable substratum for colonizing microorganisms. XRD analyses indicate mainly the presence of quartz, sodic and/or calcosodic feldspars. There is also a scarce quantity of iron oxides (hematite) and probable contents of limestone and potasic feldspars in low proportions, as well as a small amount of clay material. SEM observations (Fig.) and EDAX microanalysis (Fig.) confirm the results obtained by XRD.

3.2 Microbiological assessment

The results of the quantitative samples are shown in the Tables 2 to 3. When comparing table 2 to table 3, it is evident that all cleaning methods were efficient to limit or eliminate the microorganisms. However, after three months microorganisms are apparently starting to grow in sections 701 and 801.

Table 2: Pretreatment and post- treatment condition (numbers express the number of CFU's)

Treatment	CFU															
	Before cleaning								After cleaning							
	24 h				48 h				24 h				48 h			
	1	2	3	Av.	1	2	3	Av.	1	2	3	Av	1	2	3	Av
601	4	5	3	4	7	8	5	6.8	0	3	0	1	5	3	0	2,66
701	7	3	5	5	9	13	5	9	0	0	0	0	0	0	0	0
801	0	7	6	4.3	100	48	125	91	0	5	1	2	1	0	8	3

Table 3: Control after a month and three months (numbers express the number of CFU's)

Treatment	1 month								3 months							
	24 h				48 h				24				48			
	1	2	3	Av	1	2	3	**Av.**	**1**	**2**	**3**	**Av**	**1**	**2**	**3**	**Av**
601	0	0	0	0	1	0	0	0.3	0	0	0	0	0	0	0	0
602	1	0	0	0.3	1	2	1	1.3	0	0	0	0	0	0	0	0
603	1	0	0	0.3	1	0	0	0.3	0	0	0	0	0	0		0
701	0	0	0	0	0	0	0	0	1	0	0	0.3	1	1	0	0.6
702	0	0	0	0	0	3	0	1	0	0	0	0	0	0	0	0
703	0	0	0	0	0	0	0	0	3	1	2	2	3	1	2	2
801	0	0	0	0	1	0	0	0.3	1	0	0	0.3	3	2	1	2
802	1	0	0	0.3	1	0	0	0.3	0	0	0	0	1	0	0	0.3
803	1	0	0	0.3	1	0	0	0.3	0	0	0	0	01	0	0	0.3

When looking at the results of surfaces treated with hydrophobes, we find no CFU or very low counts, and no differences or trends can be noticed in the effect of both hydrophobes, except in section 703 where microorganisms seem to be growing again.

As regards hydrojet washing, there were colonies growing after the cleaning in section 601, but that trend did not continue in the following controls.

As for the bricks exposed in the apse´s roof, after three months very small colonies of Chlorococcal algae could be observed in the one treated with hydrophobe 1, whereas no signs of new organisms could be seen in the brick treated with hydrophobe 2.

4 Conclusions

The physical tests showed the bricks of La Plata Cathedral are very porous, and retain water for a rather long time (a week up to ten days) in humid conditions. This condition is suitable for the growth of microorganisms, although in this case, the original microbiological counts were low. This explains why biofilms grow in the areas more exposed to rainfall and less exposed to sun, and is very important for the survival of microorganisms if we consider that there was a decrease in the amount of rainfalls during the last decade, with 2008 as the driest year.

It is also important to notice that, according to results of the natural humidity tests at different depths, the water uptake is mainly by capillary absorption of ground water.

The methods of cleaning reduced the number of microorganisms or directly, eliminated them. The exception was the cleaning with neutral detergent: at first, there was almost no growth of new microorganisms, because the section was sprayed with sodium hypochlorite prior to the final rinsing with water, but after three months, colonies are detected in the untreated section. This is because sodium hypochlorite has no residual effect. In contrast, the sections treated with hydrophobes are still clean.

This also happens in section 701, only cleaned with sodium hypochlorite: after three months, there is growth of microorganisms although in very low numbers. It is indeed remarkable that section 703, treated with hydrophobe 2, also shows the presence of new colonies

Follow up visual inspections and quantitative sampling of microorganisms in the cleaned walls and the bricks exposed in the apse's roof showed in the short term (1- 3 months) that there is almost no growth in the treated surfaces whereas the untreated surfaces had low microbial counts, and no difference in the action of the hydrophobes can be observed. Longer term inspections will be carried out to determine if this trend lasts.

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