

Trials of biocide cleaning agents on Sydney sandstone

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TRIALS OF BIOCIDES CLEANING AGENTS ON SYDNEY SANDSTONE

Introduction

The project sought to test:

- the relative efficacy of two commercially available biocides on local sandstones in the Sydney climate;
- the effect of different application conditions and methods, specifically pre-wetting and brush or poultice application;
- the period of residual effectiveness on local sandstone in Sydney.

The project also sought to test the conclusions of a past study (Charola et al, 2012) which found that biocides were effective at removing bio-colonisation and that their application in conjunction with scrubbing and/or pre-wetting was even more effective. Given the relative lack of durability of Sydney sandstones, the present study sought to establish whether acceptable levels of cleaning could be achieved without scrubbing.

A proposal for biocide trials was first developed for the NSW Public Works Centennial Stone Program and the opportunity arose to try an amended scheme on the Museum of Contemporary Art building in Sydney.

Building History

The Museum of Contemporary Art building was originally constructed as the offices of the Maritime Services Board, at Circular Quay. Designed in the late 1930s, demolition work began briefly on site in late 1939 and stopped in July 1940. Works began again after the war and the building was officially opened in December 1952. It was converted into the Museum of

Contemporary Art, opening in 1991, with some significant additions. Further additions were made in 2011.

The building was constructed of sandstone quarried from the State Government Quarry at Maroubra, Sydney. Sandstones of the Sydney region are generally classed as 'argillaceous', that is, having significant amounts of clay in the binding matrix. Samples of Maroubra Sandstone have been shown to contain 15-22 % clay (Franklin, 2000). The high clay content in the matrix generally correlates with lesser durability.

Project background

This investigation into biocide cleaning agents was prompted by cleaning the exterior in 2012 and 2013. The work had been specified to include cleaning with water under low pressure, subject to site trials. During the works, despite repeated interventions by the conservation staff inspecting the works, it appeared that the pressure was too high for the surface, as evidenced by the amount of sand (from the stone surfaces) in the wash water.

The building had been cleaned previously in 2002 using water under high pressure, the specification said "nominally 2000 psi". While this would have been the pressure provided by the pump, the pressure of the water delivered to the surface would have been less. However, even an eighth of this pressure on the surface would have been sufficient to cause damage to this type of stone.

A review of photographs from the time of construction until 2012 suggested a very slow build up in biological growth from 1952, as the stone weathered and the surface became more open. Dark patches in areas of water run off first become noticeable in relatively small areas the 1980s.

The review of photographs also suggested that the biological regrowth became more extensive, that is darker and over larger areas, *after* the cleaning programme in 2002 than it had been before.

By 2012, the stone had again become very streaked and dark on the upper wall surfaces and parapets, with growths more extensive on the southern surfaces.

Concern about the rapid regrowth since 2002, the loss of surface grains when cleaned and the ongoing effect of cleaning at ever shorter intervals led to a review of the approach to cleaning sandstone and other methods of controlling micro-biological growths.

Biocides, chemical compounds which kill or control micro-biological growth, are an accepted part of stone conservation at an international level. The most common active ingredient of biocidal agents for masonry is benzalkonium chloride, which is also a common ingredient in domestic disinfectants and swimming pool algacides. Benzalkonium chloride is a quaternary ammonium compound, which are also known as 'quats'. They are used at very low dilution rates, e.g. 2% in water (Caneva, et al., 2008; Nugari & Salvadori, 2003).

Investigation into biofilms on the building

A biofilm is a conglomerate of various microbiological growths usually beginning with bacterial colonists which secrete substances that form a gelatinous film or slime on or within which other types of microbiological growths can attach and start growing. When wet, biofilms feel slimy to touch.

Before applying biocides, the biofilms on the building were reviewed in-situ by a botanist. It was found that the growths varied over the upper surfaces of the building. Red and green algae and various types of lichens, were identified (Archer, pers. comm.). Detailed in-situ photographs were taken of the biofilm and scrapings were investigated under a optical microscope.

Location of trials

The trials were applied to the inside of the parapet walls of a roof-top balcony on the north-east corner of the building (Figure 1). The choice was driven by the presence of significant levels of biological growth which were easily accessible for both application and monitoring, and which would not affect the outwards appearance of the building for the period that the trials were underway. The trials were applied to three parapet walls so that the effect of different orientations could be observed.



Figure 1 View looking north over the northern balcony of the Museum of Contemporary Art building. Trials were conducted on the inside faces of the very large parapet stones to the north, east and south walls of the balcony.

Biocides

Two biocides that are common on the Australian market were trialled:

1. Wet and Forget

This product is supplied as a blue liquid concentrate in which the active ingredient is benzalkonium chloride. The concentrate was diluted on-site to produce a 2% solution (i.e. 20 grams per litre).

2. Boracol 100RH

This product is supplied as an already diluted clear liquid. The active ingredients are benzalkonium chloride present at a rate of 22g/L, and boron present at a rate of 23g/L.

Methodology

The methodology provided for the application of both biocides by brush with three different surface conditions:

- pre-wet with water on the day of application;
- double pre-wet with water: i.e. on the day before application and on the day of application;
- no pre-wetting, i.e. the biocide applied to a dry surface.

One of the biocides was also applied within an absorbent paper poultice, Westox 'Cocoon', which is normally used for desalination. The aim of testing the use of the poultice was to assess whether the longer contact time improved the effectiveness of the treatment. The same three surface conditions: single pre-wet, double pre-wet and dry were used with the poultice applications.

The ethylene glycol solvent used in Boracol was also added to one trial of Wet and Forget to test whether the solvent improved the biocidal effect. Ethylene glycol is also used as a fungicide, particularly for treating rot in timber. Isopropyl alcohol was added to another of the Wet and Forget trials to test whether its presence improved penetration of the biofilm.

The table below sets out the different biocides, application methods and surface conditions. The complete scheme was applied three times, once each to the north and south walls in 0.5 metre wide panels, and once to the east wall in one metre wide panels. Untreated control panels were left at the end of each wall and were included in the middle of the range of trial panels. Poultices were covered with cling film for five days and then allowed to dry naturally. All the trial panels were kept covered for 14 days to prevent them being affected by rain. The poultices were taken off when the coverings were removed.

Biocide trials testing scheme			
No	Biocide	Application	Surface condition
1	Wet and Forget	brush	dry
2	Wet and Forget	brush	single pre-wet
3	Wet and Forget	brush	double pre-wet
4	Wet and Forget	Cocoon poultice	double pre-wet
5	Wet and Forget	Cocoon poultice	single pre-wet
6	Wet and Forget	Cocoon poultice	dry
7	Control	—	—
8	Boracol 100RH	brush	dry
9	Boracol 100RH	brush	single pre-wet
10	Boracol 100RH	brush	double pre-wet
11	Wet and Forget + 10% Ethylene Glycol	brush	double pre-wet
12	Wet and Forget + 10% Isopropyl Alcohol	brush	double pre-wet
13	Wet and Forget	brush	double pre-wet

Table showing testing scheme of biocides, application methods and surface conditions. The complete scheme was applied to each of the three parapet walls of the balcony (Figure 1).

Monitoring and recording of trials

The trials have now been monitored and reviewed for 2.5 years (30 months). Observations made at approximately six-month intervals have included visual inspections and digital photography. A field microscope has been used to assess whether there has been any regrowth.



Figure 2 The eastern wall of the balcony, 23 months after treatment. The dark area left of centre is the untreated control panel; to its left are panels treated by poultice application of biocide. Note the wide zones around the mortar joints showing a biocidal effect, and the evidence of previous cleaning in the form of horizontal bands from pressure-washing.

Complicating factors

A range of factors have influenced the appearance of the trial panels and complicate assessment of the results. These include:

- orientation of the trial panels, which face north, west and south, leading to different micro-environmental conditions for the biological growths, and different photographic recording conditions, both making comparison between walls difficult;
- the influence of mortar joints — alkalinity from the mortars has had a biocidal effect which extends some distance from the joints (Figure 2);

- run-off from the horizontal top of the parapet which intensifies growths in some locations, and may be contributing to regrowth;
- previous cleaning — now visible as horizontal bands from pressure-washing (Figure 2);
- other treatments — which have left various marks on the stone surfaces, some of which have become apparent only after the cleaning trials have removed much of the biofilm;
- location of trial panels close the walls of the main building — which has resulted in less-effective cleaning due to additional water run-off and splash from the wall surfaces;
- untreated control panels have continued to accumulate biological growths, increasing the contrast between treated and untreated panels, and so complicating assessment of the degree of cleaning achieved (Figure 5).

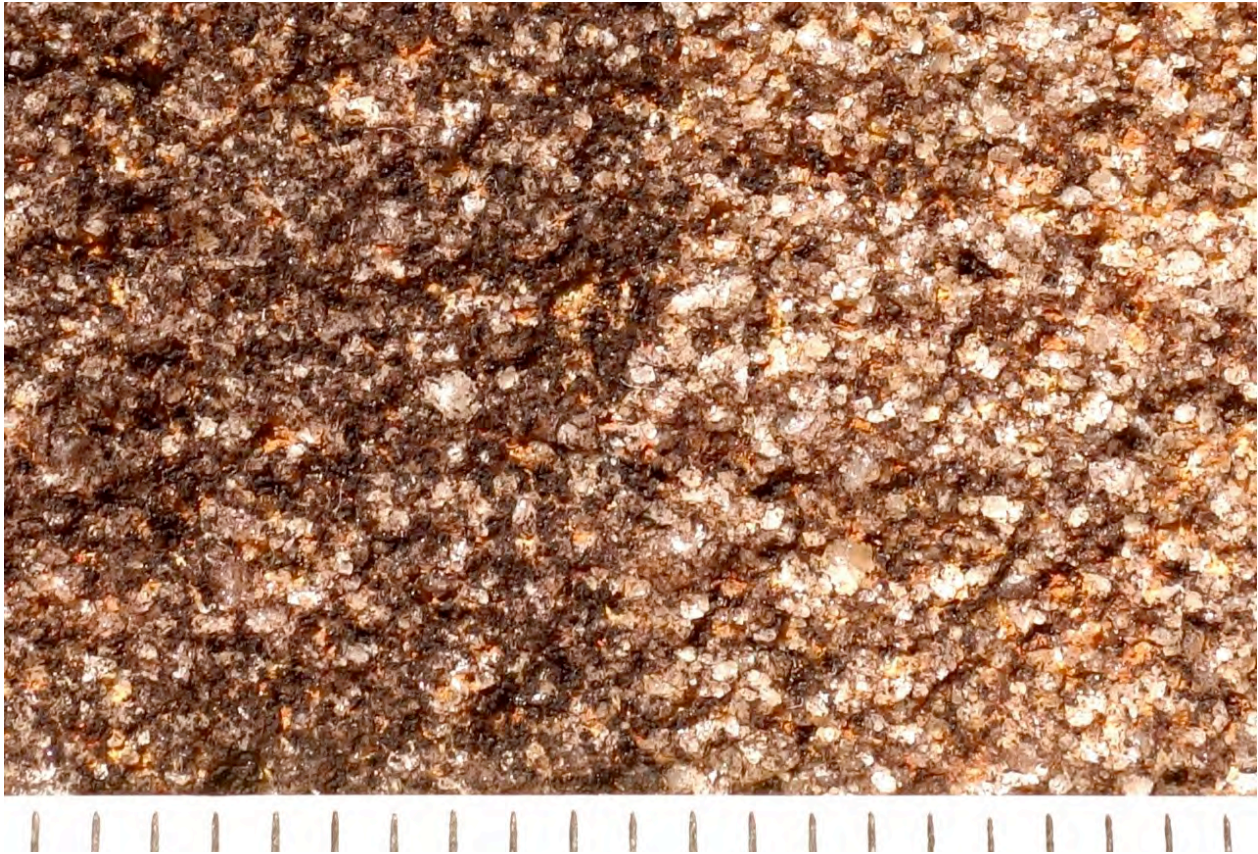


Figure 3 Close-up photograph showing untreated control at left, and to the right an area treated by brush application of Boracol 100RH. Scale bar is in millimetres. Note how the biofilm covers a large proportion of the stone surface at left, while on the right the treated area retains residues of the biofilm. Orange-coloured particles are iron-stained clays (see Figure 4). Photograph taken 23 months after treatment.

Results

Bearing in mind the complicating factors, the following results have been found:

- both biocides were effective in controlling the biofilm (Figures 3 and 4), with little discernible difference between the two, and little or no loss of surface from the sandstone;
- separate additions of ethylene glycol and isopropyl alcohol to one of the biocides show no discernible differences;
- prewetting in this instance does not seem to have increased the efficacy of the biocides;
- the cleaning effect of the treatments continued to improve for at least eleven months after treatment, and is retained at 23 months;
- poultice applications were more effective than any of the brush-applied biocides;
- poultice applications left a residue which washed off most areas within one year, though residues can still be seen with a field microscope after two years;
- untreated control panels have continued to accumulate biological growths.

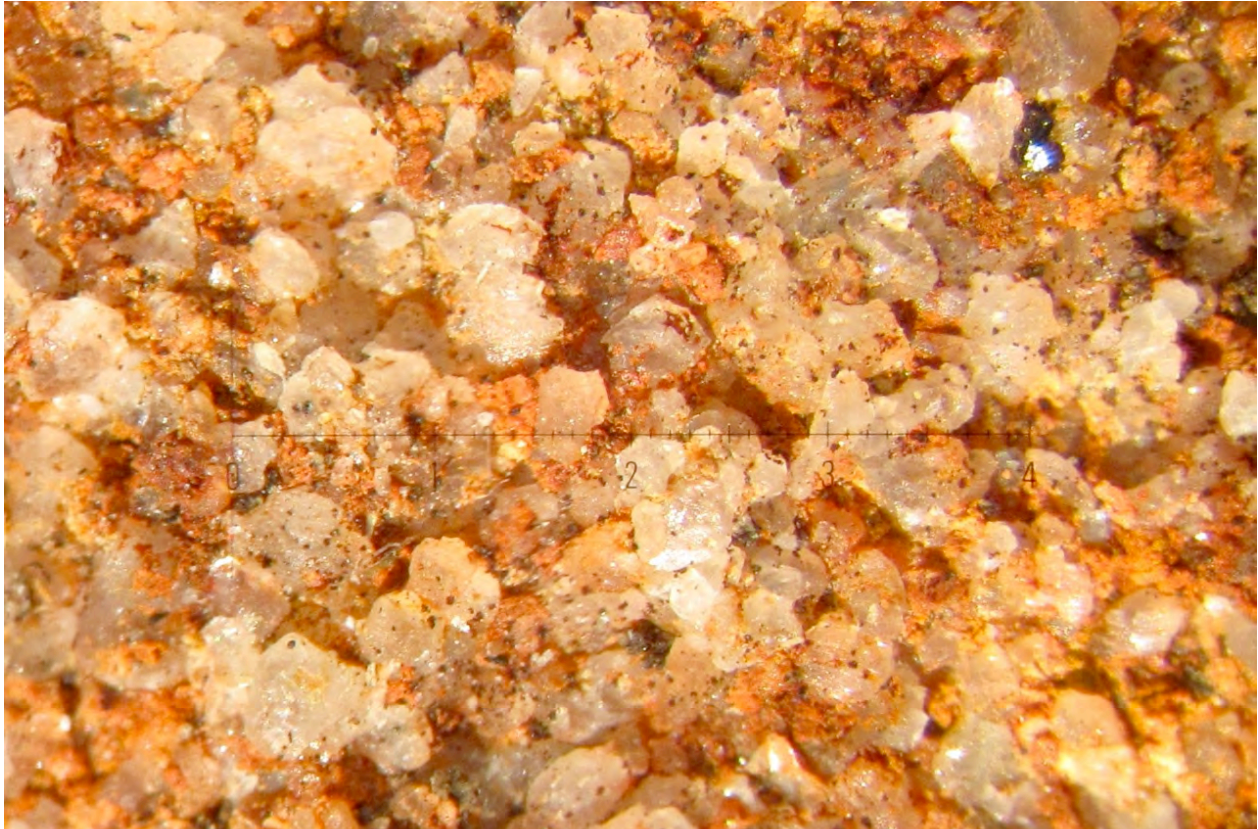


Figure 4 Microphotograph of cleaned sandstone; the scale is in millimetres, small divisions are tenths of a millimetre. Small black ‘dots’ visible on light-grey quartz (sand) grains are what remains of the biofilm. Bright orange-coloured particles are iron-oxide stained clay minerals which give the characteristic colour to ‘yellow-block’ sandstone.

Discussion

Following completion of the biocide applications, all treatments were left untouched so that any residual effects and changes over time would become apparent. As observed by Charola et al. (2012), the cleaning effect continued to improve for at least eleven months after treatment. Figure 5 shows a sequence of images, which demonstrate improvement in both poultice and brush applications at eleven months.

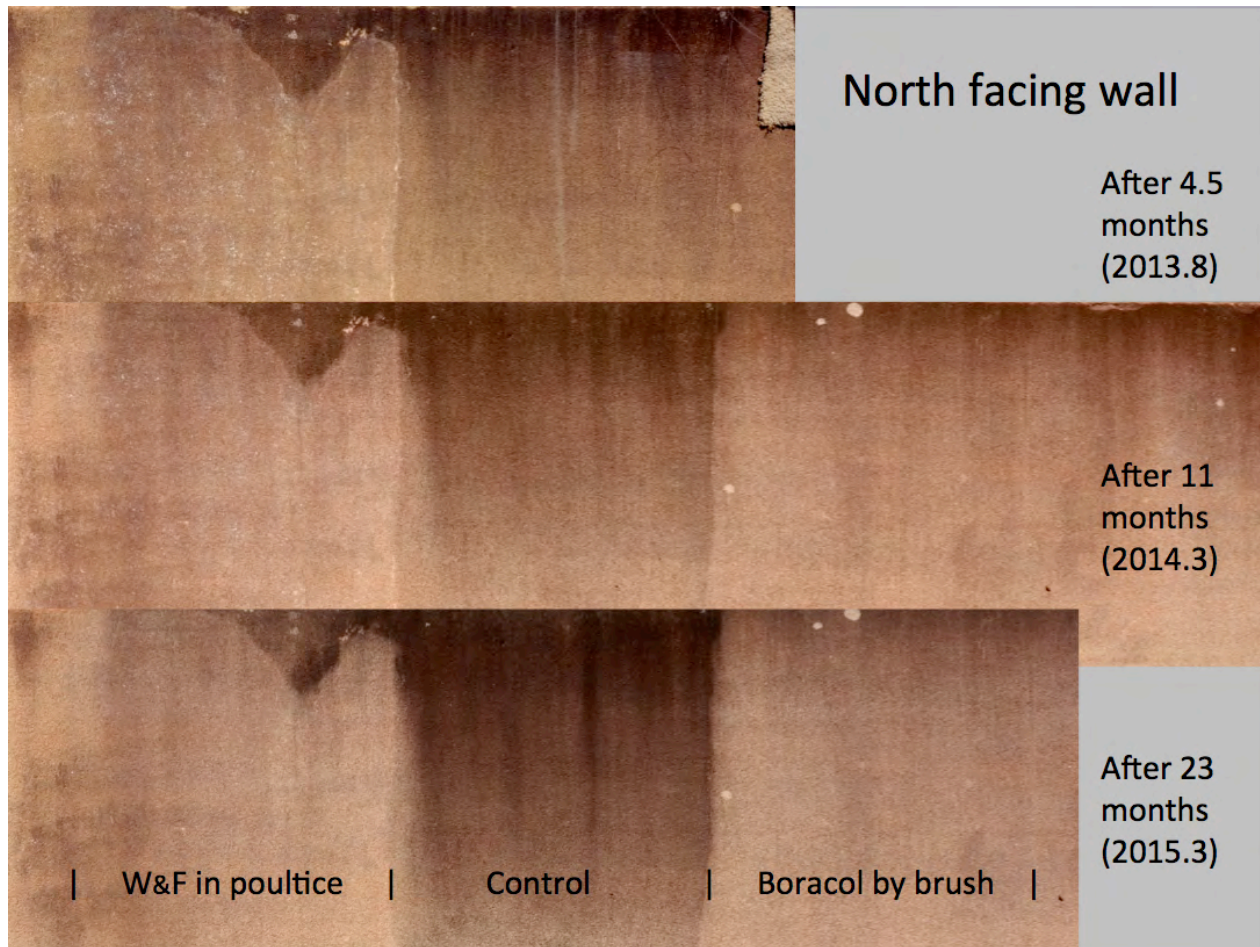


Figure 5 Sequence of images taken 4.5, 11 and 23 months after treatment, of a section of the south wall. The cleaning effect of the two treatments shown is similar, both improving until at least eleven months (but compare with Figure 6). Note the white residue from the paper poultice at left, which washes off with time; and the intensification of the dark biofilm in the untreated control panel.

Also apparent in Figure 5 is a white residue from the paper poultice, which is still visible after eleven months, but is almost gone at 23 months. Such a residue would not be acceptable in a full scale cleaning project, and so further trials should test different clean-up procedures and their timing.

It might be inferred from Figure 5 that there is little difference between the application of one biocide by poultice, and the other by brush. However, Figure 6 shows an image of the same set of panels from the opposite (south-facing) wall, taken 23 months after treatment. Here there is a clear difference between the cleaning effect of the poultice application compared to that applied by brush. A similar result was found on the west-facing wall.

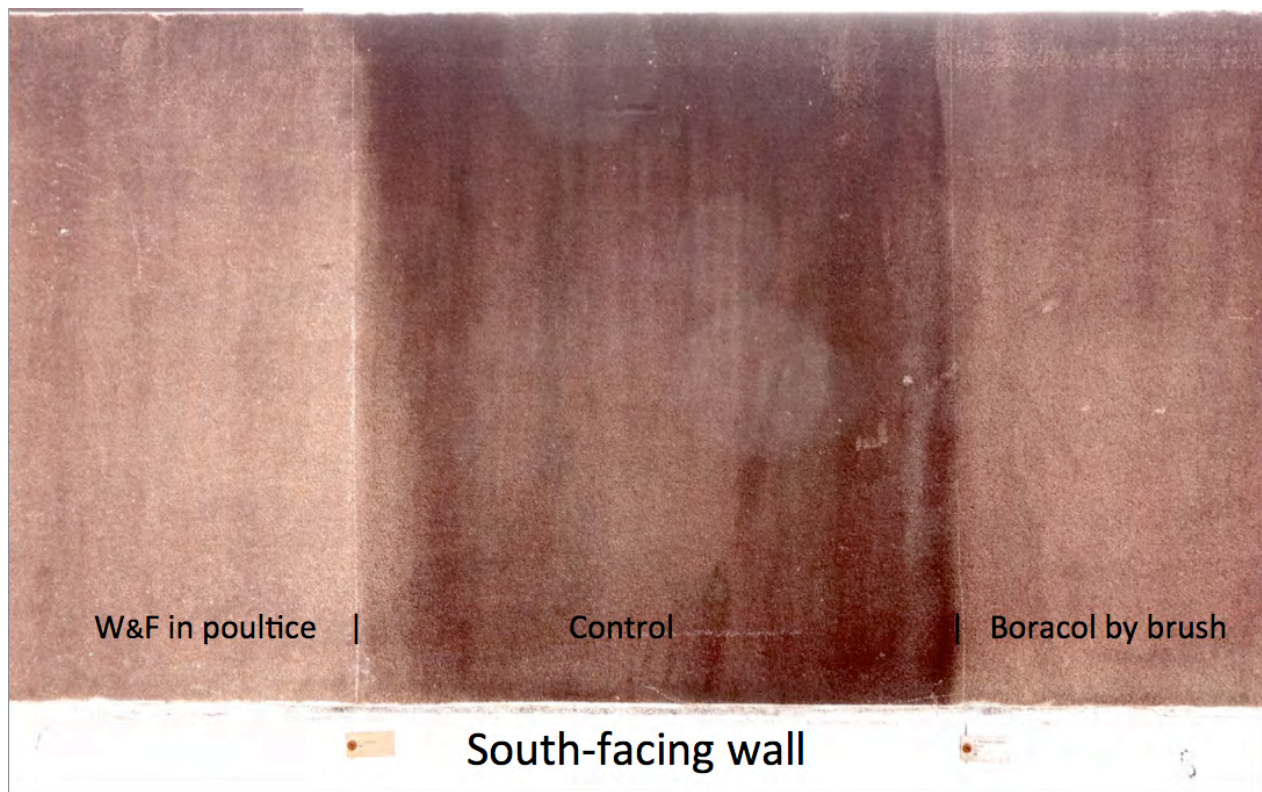


Figure 6 The same set of trials as in Figure 5, but on the north wall, showing that the poultice application is more effective than brush application. Similar results were found on the east wall. Photograph taken into the sun, 23 months after treatment.

Why is the poultice application apparently more effective? There may be several answers to this question. One possibility is the longer dwell time that the poultice provides. The biofilm is quite slimy and resists penetration, so longer contact times may be a key factor.

Another possible explanation is that, although the dilution rates for the biocides applied by brush and by poultice were approximately the same, the poultice application may have resulted in more biocide being delivered per unit area than was the case by brush. Further trials should seek to test this, by ensuring that the same amount of biocide is applied whichever application method is used, and by trialling double and perhaps triple applications by brush. Related to this is the argillaceous (clayey) nature of the sandstone (Figure 4). As clay minerals absorb some of the quaternary ammonium compound, argillaceous sandstones may require more biocide for it to be effective, but its effect may last for longer (Salvadori, pers. comm.). Application by poultice may have been more effective at delivering biocide to the clay-rich sandstone.

As Figure 3 shows, brush application of the biocide has clearly had an effect on the biofilm, yet there is a substantial quantity of remnant biological material on the surface. Though degraded, there is a risk that this material will provide a food source for a future biofilm, and so further tests should look at ways of removing the residue. Among the methods that should be trialled are: additional applications of biocide; clean-up after a period of four weeks using, low pressure washing, captive-head washing, and light scrubbing, with and without a further application of biocide, the latter being used for both its biocidal and detergency properties.

While Charola et al. (2012) found that pre-wetting the surfaces had a beneficial effect, these trials did not show the same results. The reason may be related to the amount of pre-wetting, which in this case was relatively light. Pre-wetting has two purposes: to 'activate' the biological growths so that they are growing well and will take up the quat; and to control the suction of the porous

stone, so that the biocide will remain close to the surface where it is needed, and not be 'lost' deeper in the stone. Future trials should test the addition of substantially more water.

Conclusions

Biocides are an effective means of controlling dark microbiological growth on sandstone buildings in the Sydney climate. Biocides offer a better means of cleaning than pressure-washing, or other abrasive methods, because the surface of the stone is not further removed by the process. Applying the biocide within a poultice improved the cleaning effect though there was some variability depending on orientation, and hence exposure, of wall surfaces. Prewetting did not improve the performance of the biocides, though this may be related to the amount of water applied in these trials and to the difficulty of penetrating the biofilm, and so may not be evidence that pre-wetting is not warranted. Future trials should seek to test:

- methods to open up the resistant biofilm prior to treatment, such as light hand scrubbing;
- more prolonged pre-wetting;
- more accurate biocide dosage rates, whether delivered by brush or in a poultice; and
- methods of post-treatment clean-up, to remove residues and inhibit future growth.

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References

- Caneva, G., Nugari, M.P. & Salvadori, O. (eds) 2008. *Plant biology for cultural heritage: biodeterioration and conservation*. Getty Conservation Institute, Los Angeles.
- Charola, A.E., Wachowiak, M., Webb, E.K., Grissom, C.A., Vicenzi, E.P., Chong, W., Szczepanowska, H. & DePriest, P. 2012. "Developing a methodology to evaluate the effectiveness of a biocide." Proceedings of the 12th International Congress on Deterioration and Conservation of Stone, Columbia University, New York.
- Franklin, B. 2000. "Sydney dimension sandstone: the value of petrography in stone selection and assessing durability". In *Sandstone city*. Proceedings of a symposium held on 7th July, 2000, during the 15th Australian Geological Convention at the University of Technology, Sydney.
- Nugari, M.P. & Salvadori, O. 2003. "Biocides and treatment of stone: limitations and future prospects." In Koestler, R.J., Koestler, V.H., Charola, A.E. & Nieto-Fernandez, F.E. (eds) *Art, biology and conservation: biodeterioration of works of art*. 518-535, The Metropolitan Museum of Art, New York.