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Durability of a Hydrophobic Product for Natural Stones Against Combined Microbiological and Chemical Stress and an Artificial Weathering Procedure

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Abstract

Weathered stones (Cotta Sandstone) were impregnated with a new, hydrophobic, PUR-based impregnation material. One series of specimens was exposed to a forcing combined chemical and microbiological attack and another series to an artificial weathering test. The reduction of capillary water absorption remained after both stress procedures. SO_2-deposition was reduced to about 50 % by the impregnation; combined microbiological and chemical stress caused a further reduction. The impregnation successfully prevented the material from strong colonisation with bacteria.

Keywords: chemical attack, microbiological attack, capillary water absorption

1 Introduction

To retard the deterioration of porous natural stones, new classes of cold curing polymer products have been developed. According to the specification concerning individual monuments, the impregnation may be hydrophobic or not [1]. The products have to prove their durability in accelerated ageing tests, which simulate the reality to a maximum degree. The investigations presented here are part of a complex research program, which is still going on and will be completed in 1999.

In case of hydrophobic impregnation materials, water permeability and water uptake are main indicators for the durability of the product. The results presented here focus on parameters characteristic for the interactions of a film-forming, hydrophobic impregnation material on Cottaer Sandstone with water after different stress conditions. Combined microbiological and chemical stress or complex artificial weathering were performed independently in different simulation chambers.

2 General plan and sample preparation

Figure 1 shows a general plan of the investigations. The diagrammatic view is a small part of an extensive investigation. Therefore the number of specimens for each parameter combination differs according to the testing

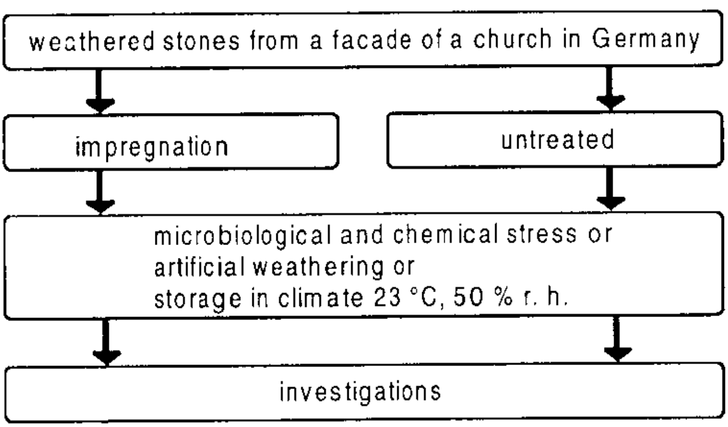

Figure 1: General plan of testing

method. The number of individual values, forming the presented result is given with the individual results in the relevant chapters.

The investigations were carried out with weathered stones from the facade of a German church (Lukaskirche near Zwickau). Among the storation work some old hewn stones from the ashlar masonry had to be substituted by freshly quarried stones. Their exposure conditions (place and time of exposition) are well known. Chemical analysis showed partially high concentrations of gypsum near the weathered surface, microbiological colonisation was rather low. In some areas the surface was discoloured by dirt; incrustation was not found.

The hewn stones were sawn into specimens of 5 cm x 5 cm x rd. 10 cm. The weathered surface was at one front side (5 cm x 5 cm). The four sides 5 cm x rd. 10 cm were sealed with an epoxy-coating.

As impregnation material a film forming, hydrophobic product based on PUR was applied in butylacetat solution. In the next chapters the product is indicated by its laboratory number 219.

The protecting agent was applied by 2h of free capillary absorption from the weathered surface of the specimen. Depending from the individuality of the specimen, the samples took up between 2 and 5 kg/m2. Before the specimen were exposed to the stress procedures they were stored at 23 °C, 50 % r. h. for 6 weeks.

3 Stress

3.1 Artificial Weathering

An artificial weathering with multiple parameters was carried out in a special test device for natural stones. Figure 2 shows a schematic plan of the experimental device. The test device is divided in two sections by a horizontal layer of specimens: climate 1 (C1) and climate 2 (C2). The upper climate presents the conditions outside a building, the lower climate presents indoor conditions. Sun (S) and rain (R) are placed in climate 1. The spectral distribution of the sun radiation is according to the international standard D65. The gases SO_2, CO_2 and NO_x are mixed and injected. They are added during well-defined times of the weathering cycle. The concentration corresponds to the German conditions of „smog, alarm 1". Both climates are independently regulated concerning humidity and temperature. The speci-

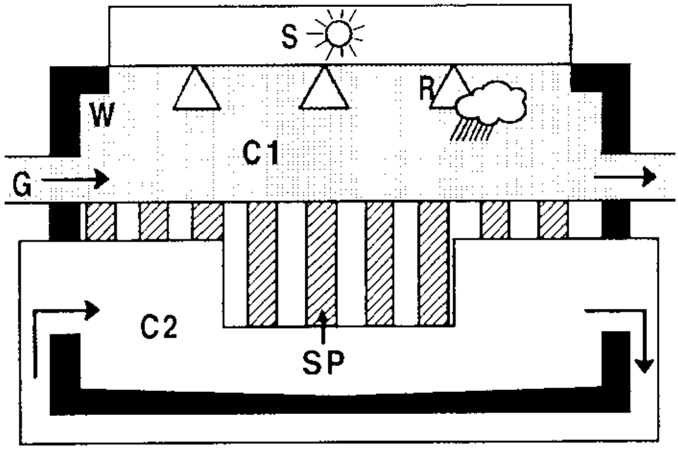

Figure 2: Schematic plan of the experimental system for artificial weathering
SP specimens, separating section 1 and 2
C1,C2 section 1, 2 (climate 1,2)
G polluted air input, wind input
S sun (IR, visible light, UV)
R water nozzles
W wall temperature independently controlled from temperature in chamber 1,2

mens (SP) sized 5 x 5 x 10 cm^3 are placed in such a way, that humidity and temperature transport can only take place vertically. The weathered surface is 5 x 5 cm^2. The temperature of the chamber walls (W) can be regulated. This allows definite condensation on the inner surfaces of the stones.

To make sure that no unnatural process of deterioration is involved, all maximum and minimum temperatures and temperature gradients were adapted to the data from different Central European meteorological stations. Acceleration is achieved by selecting those parameters which are most important for the deterioration. These parameters are combined in a special way and form a cycle of one week. This week presents all the extreme, but real weather elements of one medium Central European year. Detailed information about the experimental device and the theoretical background are described in [2].

The specimens were weathered in the test device for 7 months.

3.2 Combined Microbiological and Chemical Stress

As there are interactions between microbiological and chemical weathering [5], a combined microbiological and chemical attack was simulated. The specimens were incubated for 12 months at 25 °C and about 90% r. H. in a climatic chamber described in [5]. A stimulation of the indigenous chemoorganotrophic microflora of the material was achieved by keeping the specimens at a stone moisture between 80 and 100 % of the maximum water holding capacity. This was achieved by periodical wetting (1 of 4 weeks) through a closed watering system filled with calcium carbonate buffered water. At the beginning of an experiment for each impregnated specimen the penetration depth of the impregnation material was estimated (by the material uptake) and each specimen was, through a drilling located at the border between impregnated and untreated material, inoculated with pure cultures of nitrifying bacteria (Figure 3). In the case of untreated specimen, the drilling was located in the middle of the specimen. Through the drilling nitrifying bacteria were weekly supplied with ammonium chloride (2 mM solution) and urea (1 mM solution) as substrate.

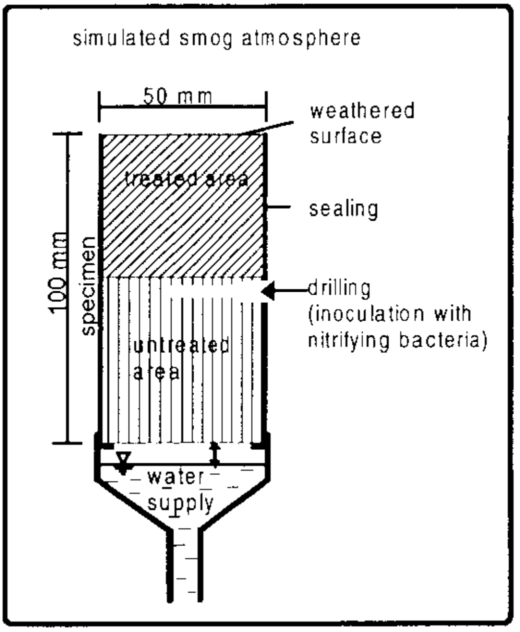

Figure 3: Test device for microbiological and chemical stress

To simulate a chemical attack, a smog atmosphere containing 400 ppbv SO_2, 400 ppbv NO_2 and 800 ppbv NO was adjusted in the chamber. These concentrations resemble maximum values occurring during smog situations.

4 Methods of investigation

4.1 Water Absorption

To evaluate the hydrophobicity the capillary water uptake through the weathered (and impregnated) front during 1 h was determined.

4.2 Water Permeability

To measure water vapour permeability, normally tests according DIN 52615 (wet -cup or dry-cup) are carried out. Usually both test methods give different results. These differences are due to the fact, that the moisture content of the specimens differs. In both cases the moisture content is in an equilibrium condition (sorption moisture content), but in case of wet-cup method in a higher range. According to the moisture content, water transport takes place not only by water vapour diffusion, but also by capillary transport. Water transport by capillary forces is more powerful. That is the reason, why diffusion resistance μ measured by wet-cup normally is lower than diffusion resistance μ, measured by dry-cup method.

Moisture contents in real facades are often much higher than the moisture contents in the diffusion tests mentioned above. Especially in case of high moisture content the water permeability is of great interest, because the dehumidification should not be affected adversely by the waterproofing agent. For this reason, the water permeability tests had not been carried out according to DIN 52615. The chosen device is schematically shown in Figure 4. The specimen were placed in a way, that the weathered (and treated) front side rises to the climate 23 °C, 50 % r. h. The sawn back side is in contact with deionized water. The water surface is sealed from the climate except of a small hole of defined size (to prevent from depression). Water is sucked by capillary forces and evaporates at the upper front side of the specimen. The flow of transported and evaporated water can be calculated by regular weighing. The amount of water, transported by diffusion through the small hole, is taken into account.

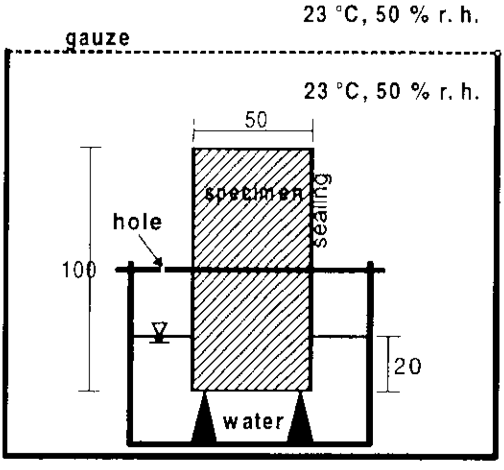

Figure 4: Test device for the determination of water permeability (dimensional unit: mm)

4.3 SO_2-Deposition

The deposition of SO_2 is depending on the stone moisture. Therefore the specimens were adjusted to the sorption moisture content at 80 % r. h. before the test was carried out. It took 6-8 weeks (untreated stones) and 10 weeks (treated stones), until the samples reached the equilibrium conditions.

To determine the SO_2 deposition, the specimens were exposed to a special atmosphere for 7 d in a reactor. The atmosphere contained the following gas concentrations:

- SO_2: 100 ppbv,
- NO_2: 100 ppbv,
- O_3: 100 ppbv.

The specimens were placed in a way, that only the weathered (and impregnated) front side of the specimens was exposed to the atmosphere. The gas concentration at the reactor entrance is regulated to a constant value. The flow rate of the gas, passing the reactor, was kept at a constant value. The concentration at the reactor exit is measured. The amount of SO_2, which deposited on the specimen, was estimated by the difference between the concentrations at the entrance and at the exit of the reactor. Principles of the experimental device are described in [3].

Deposition of SO_2 means the amount of SO_2, which is absorbed by a defined area in a defined time. The dimension is (in SI): kg/(m^2s). SO_2-deposition in relation to the concentration of the absorbed gas in the atmosphere leads to the dimension (kg m^3) / (kg m^2 s) = m/s; the so-called velocity of deposition. Common velocities of SO_2 -deposition in case of fresh stones from the quarry are in the range of 0,2 to 0,5 cm/s in case of sandstone and 0,2 to 0,5 cm/s in case of limestone [4]. Velocities of SO_2- deposition in case of weathered stones were not published until now.

Three specimens (of same parameters) were measured in the reactor at the same time. Therefore the data, presented in chapter 5, are mean values for a set of 3 specimens each.

4.4 Microflora Characterisation

Cell numbers of chemoorganotrophic bacteria were determined by plate counts on DEV-gelatine agar (Merck No. 1.10685) containing 0,1 mg/l Nystatin to suppress growth of fungi. Fungi were counted on SABOURAUD-maltose agar (Merck No. 1.05439) containing 40 mg/l Streptomycin and 125 mg/l Ampicillin to suppress the growth of bacteria. Both agars were diluted tenfold. Cell numbers of nitrifying bacteria were counted by a three-tube **m**ost **p**robable **n**umber test (MPN) from serial dilutions of a stone suspension. Nitrite/nitrate and ammonium contents of the stone were determined by high-performance liquid chromatography after elution (1 g / 10 ml) with deionized water or 1 M KCl-solution, respectively.

5 Experimental results and discussion

5.1 Capillary Water Absorption

Investigations of the capillary water absorption were carried out before and after impregnation or before and after stress procedure. Because the specimens had been prepared from real weathered stones, the absolute values differ a lot. Therefore Figure 5 shows capillary water absorption in % of the untreated samples before stress procedure. The absolute values of these specimens (in Figure 5: 100 %) vary from 2 to 4 kg/m^2 in 1 h (corresponding to 100 % in Figure 5).

The capillary water absorption of the untreated samples had been reduced slightly by the artificial weathering. This can be caused by modifica-

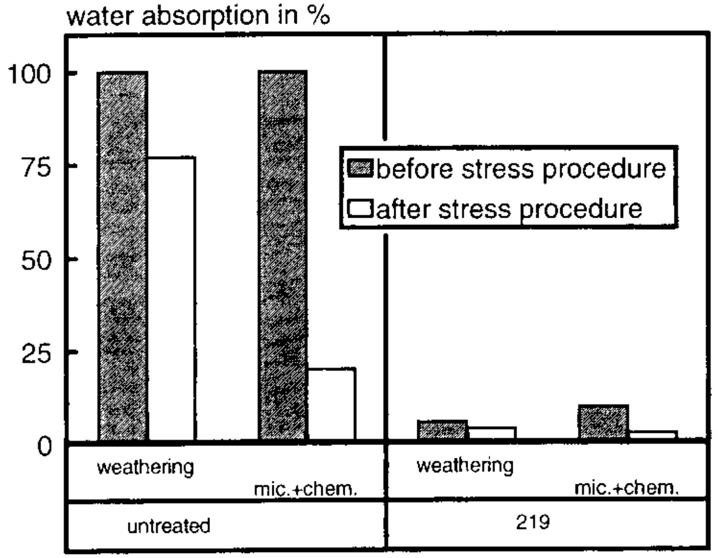

Figure 5: Capillary water absorption of untreated and treated (219) Cottaer Sandstone after different stress procedures. (weathering: artificial weathering; mic.+chem.: microbiological and chemical stress)

tion of the pore sizes by replacement of salt or new formation of salt. Incrustation of salt could be found at the lower front side of the samples (not exposed to rain, see Figure 2) after stress procedure. The salt could be identified as gypsum by X-ray inspection. This finding indicates a moisture transport from the upper (weathered and rain-exposed) front side to the lower front side of the specimens. Impregnated samples did not show incrustations.

The combined microbiological and chemical stress caused a clear reduction of the capillary water absorption of untreated samples. This is likely to be caused by the strong microbiological contamination with bacteria and fungi, which may have closed the open pores of the material. Growth of fungi was clearly visible at the weathered surface of the specimens. Additional enrichment with gypsum during combined microbiological and chemical weathering may have contributed to this effect.

The impregnation strongly reduced the capillary water absorption to 5-10 % of the basic value. This reduction remained, both after the artificial weathering and also after the combined microbiological and chemical stress.

5.2 Water Permeability

Because of the tight time-schedule, water permeability before and after impregnation or stress procedures could not be measured at identical samples in every case. Clear effects can only be stated, if the scatter ranges of the different sample groups do not overlap. Figure 6 shows scatter ranges and average values of water permeability for different parameters. The number of individual values is indicated.

Water permeability of untreated samples did not change by the artificial weathering. In contrast to that a combined microbiological and chemical stress caused a reduction to less than half of the basic value. We conclude that this is caused by a reduction of the permeability by strong microbial colonisation (see 5.1). Furthermore additional gypsum had been formed near the surface through deposition of SO_2 from the smog atmosphere (see 3.2.). This may have contributed to the reduction of the pore size near the surface.

The impregnation caused a strong reduction of the water permeability to about 5 % of the basic value. The water vapour resistance μ (measured by wet-cup) is only doubled, as known from former investigations [6]. Therefore it can be assumed, that the dehumidification of a wall with high moisture

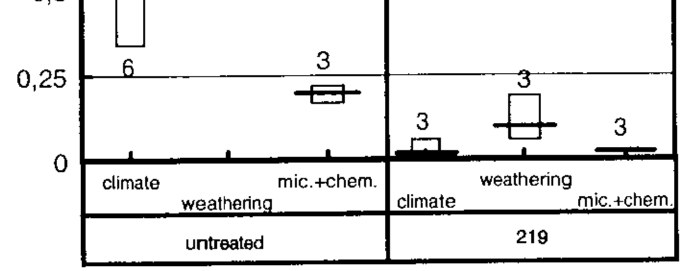

Figure 6: Water permeability of untreated and treated (219) Cottaer Sandstone after different stress procedures. (weathering: artificial weathering; mic.+chem.: microbiological and chemical stress)

content at the rear wall or inside the stone is impaired more than suspected before.

By the artificial weathering the water permeability increased again from about 5 % to about 15 % of the basic value. After the application the solvent of the impregnation material evaporates and during this transport process carries small parts of the product back to the visible surface, where they concentrate and partially close the pores. As the polymer is not UV-stable the very thin film at the surface weathers away. This effect is limited to the surface, the hydrophobic effect remains unchanged (see Figure 5). In case of a combined microbiological and chemical stress (incubation in the dark) the weathering of the polymer by UV-light was missing and consequently the water permeability of the treated samples remained at a very low level.

5.3 SO_2-Deposition

Like water permeability, SO_2-deposition could not in every case be measured at identical samples. Figure 7 shows the results for the same specimen as in Figure 6, including scatter ranges, average values and the number of

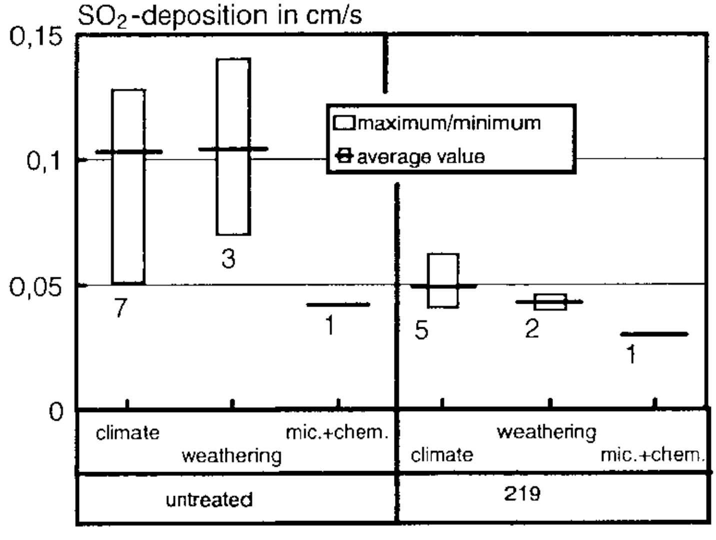

Figure 7: Velocity of SO_2-deposition of untreated and treated (219) Cottaer Sandstone after different stress procedures. (weathering: artificial weathering; mic.+chem.: microbiological and chemical stress)

individual values. As described in 4.3, each individual value represents three specimen of one parameter combination.

In case of untreated stones, the velocity of SO_2-deposition did not change by artificial weathering. Microbiological colonisation and formation of gypsum caused by the combined microbiological and chemical weathering seemed to reduce the SO_2-deposition. However, until now, only one group of three specimens has been measured. This group had also been measured before microbiological and chemical stress and its velocity of SO_2-deposition with 0,051 cm/s was at the lower limit of the scatter range. Therefore more tests have to be carried out to verify the mentioned trend. The impregnation caused a reduction of the velocity of SO_2-deposition to about 50 % of the basic value. This reduction remained after artificial weathering although some adhering polymer had been weathered away (see 5.2). SO_2-deposition is known as an important contribution to the deterioration of natural stones [7]. Therefore the reduction is welcome. Microbiological and chemical stress caused a further reduction of the velocity of SO_2-deposition. This effect has most likely been caused by deposition of sulfur dioxide on the treated stone surface during combined microbiological and chemical weathering. Deposition of SO_2 may lower the surface pH and cause enrichment of gypsum which both reduces the SO_2 deposition-velocity. As only fungi were found in high cell numbers within the treated zone of the material, microbiological colonisation should be of minor importance for this effect.

5.4 Microbial Colonisation

Figure 8 shows the distribution of chemoorganotrophic bacteria with depth for an untreated and a treated specimen after 12 months of combined microbiological and chemical stress. The results for the specimen given in Figure 8 are typical for samples with the same parameter combination. Because for each specimen the penetration depth of the impregnation was different, average values for all three replica do not show how clear the distribution of bacteria was affected by the treatment. The impregnated zone of the specimens was hardly colonised by chemoorganotrophic bacteria. In contrast to this, the untreated specimens were strongly colonized with chemoorganotrophic bacteria over the whole length. Nitrifying bacteria did not colonise the impregnated zone of the material, too. In contrast to that, high cell numbers of fungi were found in impregnated as well as untreated zones.

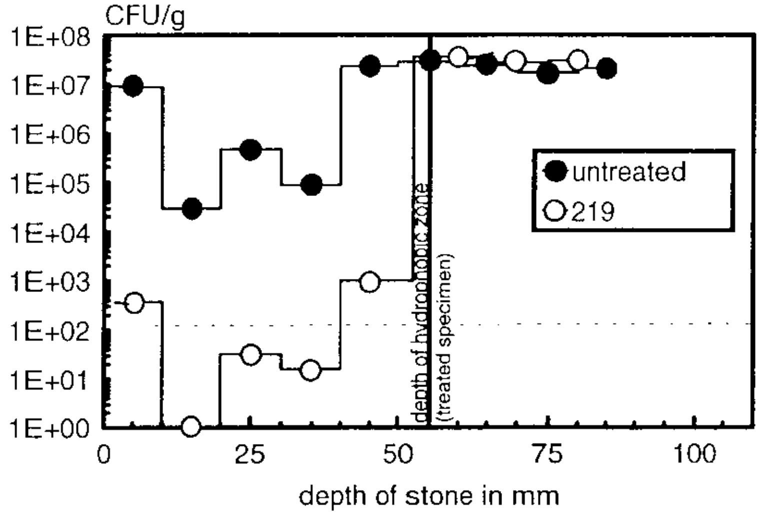

Figure 8: Cell numbers of chemoorganotrophic bacteria in an untreated and impregnated (219) specimen after 12 month of combined microbiological and chemical stress.
The dotted line indicates the threshold of the plate count technique. CFU = colony forming units.

6 Summary

Weathered stones (type: Cotta Sandstone) from a church in Eastern Germany had been impregnated with a new, hydrophobic, PUR-based impregnation material. Impregnated specimens were during 12 months exposed to a forcing chemical and microbiological attack or during 7 months exposed to an artificial weathering.

The application of two different weathering tests aimed at testing the durability of the impregnation materials against chemical, microbiological and physical factors of weathering. The parameters during testing did not exceed natural conditions.

Capillary water absorption, water permeability in case of water at the rear face of the stones (dehumidification) and SO_2-deposition were determined for treated and untreated specimens before and after stress procedures. For dehumidification a new test is presented, which turned out to be a good complement to DIN 52615. After this non-destructive testing, specimens were broken. For each series of specimens the distribution of endolithic microorganisms with depth was characterized at the end of the experiment.

The treatment with the hydrophobic impregnation material caused a strong reduction of capillary water absorption and dehumidification, compared to the untreated stone.

This reduction remained after combined microbiological and chemical attack as well as after artificial weathering. SO_2-deposition was reduced to about 50 % of the untreated material by the impregnation. Combined microbiological and chemical weathering caused a further reduction of the SO_2-deposition. The impregnation prevented the material from strong colonisation with bacteria.

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