Construction and Building Materials 70 (2014) 97–103

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Modification and modeling of water ingress in limestone after application of a biocalcification treatment

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HIGHLIGHTS

- Untreated and bio-treated samples of building limestone were subjected to water imbibition tests.
- Changes to the water transfer properties of the stone, attributable to the bio-treatment, were measured and quantified.
- A model for water transfer under these conditions is proposed, differing from the standard Washburn law.
- Bio-treatment has a limited service life over the period of the experimental run.

ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form 30 June 2014
Accepted 16 July 2014
Available online 20 August 2014

Keywords:
Historical limestone
Biomineralization
Water transfer
Imbibition
Non-linear diffusion

ABSTRACT

Water transfers have been recognized as the main vectors of alteration and are responsible for pore network modifications in building stone. Among the techniques used to limit or stop the penetration of water into the stone, the calcification properties of bacteria have been investigated and used to treat buildings. In this article we study the effect of such a treatment following a protocol used *in situ*. The effects of this biotreatment on limestone (here tuffeau) were measured over a large number of drying–imbibition cycles. As the imbibition curves did not follow the usual Washburn law, a model based on a space-dependent permeability coefficient is proposed. It leads to a non-linear diffusion model which accounts for the deviation from the standard Washburn model.

1. Introduction

The causes of building stone decay are both numerous and varied, covering physical, chemical and biological actions [1–3]. Among the most devastating causes, air pollution, salts and biodeterioration are the most frequently cited in the recent literature (e.g. [1] and references therein). The feature common to these three mechanisms is the presence of water and/or the causal role of water transfers (liquid and gas phases). The action of water within the stones is notably exacerbated by the "time of wetness" and the "time of deep wetness" as noted recently by McCabe et al. [4] due to more prolonged periods of winter wetness associated with climate changes. As water is involved in many types of stone decay [1], different surface treatments aimed at avoiding or limiting these fluxes of liquid water [5,6] have been developed. The most widely used are water repellents that form a film at the surface of the stone and hence exert a protective action ([1] and references therein). They give rather good results for low porosity stone as liquid water ingress is strongly limited and water impacting the stone surface drips down without causing damage [7]. However, for high porosity stones, the water repellents penetrate the pores, completely filling them up [8]. This is a real problem because gaseous and liquid water inside the stone can no longer escape but remains trapped within the porous lattice, just behind the water-repellent film, inducing alteration by frost damage for example [6,9,7]. This leads to aesthetic problems and in extreme cases poses the problem of the solidity of the monument.

It is therefore necessary to prevent the intrusion of water into the stone but it is also crucial to maintain a gaseous exchange between the stone and its environment [6]. In addition, physico-chemical compatibility with the treated surface is also required. For such a goal other treatments have been proposed such as organic treatments [10]. Once the role of bacteria in carbonatogenesis had been recognized, the idea was to use this property for the

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http://dx.doi.org/10.1016/j.conbuildmat.2014.07.038
0950-0618/

bioremediation of stone surfaces in historical buildings [11–13]. One of these bioprocesses creates a calcite biocoating, the nature of which is appropriate to the substrate itself [14]. The so-called Microbially Induced Carbonate Precipitation (MICP) has been studied by several groups with the aim of reducing the surface porosity of the stones ([15] and references therein). As a result, gaseous exchange from the inside to the outside of the stone is still possible while water transfer from the outside to the inside of the stone is reduced [16].

In order to reproduce as closely as possible the real conditions of applications on monuments, in this study the stones were sprayed by a treatment (*i.e.* in accordance with industrial requirements) and not immersed within the treatment solution [15]. Laboratory treatment by immersion is favorable to bacterial development but is unexploitable in situ by stone restorers. To our knowledge only a few studies have been conducted using spraying to treat the surface stone [14]. We selected an industrial protocol developed by the Biocalcite Concept company. The aim of this treatment is to create a calcite biocoating by the bacterium *Bacillus Cereus* [17,16] that partially fills the pores at the stone surface. This protocol was developed mainly to protect building limestones. The creators of this process claim that their coating "ensures the protection of limestones by restricting exchange between the interior of the rock inside and external atmosphere and, additionally, by limiting the penetration of degrading agents into the stone" [16]. This process is therefore rather unclassifiable amongst stone treatment tools: on the one hand, it is not a consolidant, neither in terms of hardness nor in terms of mechanical resistance; on the other hand, it is not a hydro-repellent either, even if the bio-coating increases the liquid water time penetration (J.F. Loubière, personal communication). Note that the choice of this bacterium is not restrictive as the nature of the bacterium does not appear to be decisive for the results; the substrate has a greater influence [14]. Like other biotreatments, the Biocalcite Concept treatment limits (but does not completely stop) the penetration of water from the exterior, while allowing gaseous fluxes in both directions.

In a previous article we characterized and analyzed the phase mineralogy produced by this biotreatment [18]. To be able to distinguish the newly formed biolayer from the substrate, the biotreatment was sprayed in the laboratory on plaster samples. The coating produced was observed by SEM, and analyzed by microprobe X and GIXD. It was shown that the composition of the coating was calcite *i.e.* a polymorphic state of calcium carbonate. The thickness of the coating was evaluated by SEM and X-ray microprobe and was found to be close to 20 μm on plasters and on a limestone [19]. Despite this result, the penetration depth of the treatment and the coating thickness are generally rather substrate dependent [20]. Nevertheless, all the stones used in the present article were the same as in [18,19] and the previously evaluated thickness remains valid.

In the present article, the objectives are to quantify the modifications in the water transfer properties due to the biotreatment and to put forward a model of water transfer on a building limestone. In situ, the hydraulic properties of building stones and/or the effects of treatments are often evaluated by the Karsten pipe method [8]. However, since the objective of this work is not only to submit the stone to wetting/drying cycles in order to test and degrade (if possible) the coating, but also to quantify hydraulic modifications of the porous media, the hydraulic measurement properties were done with the imbibition method [21]. It should be mentioned that imbibition is very aggressive for the treatment, giving a lower limit of coating resistance.

The paper is organized as follows. Section 2 describes the biotreatment and the stones on which it was applied. It presents the protocol and the method used to characterize the water properties. Section 3 discusses the experimental results and proposes a model to recover them. Finally, Section 4 presents the conclusions that can be drawn from this work.

2. Materials and methods

2.1. Material and biotreatment

The material support for the biotreatment used in this article is a tuffeau stone [22] that was collected in a quarry located near the village of Saint-Cyr-en-Bourg (France). In the past, this stone was used to build most houses, churches, cathedrals and chateaux along the Loire valley. It is a rather soft stone and is therefore an easily workable building material. Nowadays, it is mainly used to restore these monuments. Tuffeau stone is a yellowish-white porous limestone, mainly composed of calcite (0.503 g g^{-1}), silica (0.452 g g^{-1}) in the form of opal cristobalite–tridymite and quartz, and some secondary minerals such as clays and micas. The total porosity of the tuffeau stone studied here was 48.1%. It is a multi-scale porous medium since the equivalent pore size distribution ranged from 0.01 to 50 μm [22].The reader is referred to the article by Beck et al. [23] for further details about the characteristics and properties of the stone.

Imbibition measurements were performed on cylindrical samples (diameter: 30 mm) that were small enough for the gravity effect to be neglected (height: 60 mm) [24]. The cylinders were all cut parallel to the sediment bedding in order to avoid undesirable anisotropic effects. Before treatment, the samples were oven-dried during 96 h at 50 °C in order to remove all residual water. They were then placed in a desiccator with phosphorous anhydrite in order to reach room temperature while maintaining a dry environment. The capillary coefficients were calculated using three samples (three for the treated and three for the untreated samples) in order to average the local inhomogeneities of the pore lattice.

The biotreatment used in this work involves a bacterium (*Bacillus cereus*) that is particularly well-suited for limestones [17,16]. This technique was patented (Calcite Bioconcept firm) and has often been used on limestones [18] since it generates a calcite coating *i.e.* a material of the same nature as the stone substrate, thus ensuring optimal compatibility. It should be mentioned that this biomineralization treatment was optimized in order to be completed within one week, which is one of the restorers' requirements.

For obvious reasons of conservation, transport and implementation on a restoration building site, the bacteria were lyophilized by the manufacturer. Fifteen hours before use on the site, the freeze-dried bacteria were re-hydrated with a nutrient solution developed by the Calcite Bioconcept firm (peptones, yeast, salts, antifungus). After this lapse of time, the culture medium was sprayed onto a statue or part of a monument (about 1 L/m^2). The bacteria were fed with a nutrient solution 24, 32, 48 and 72 h after spraying. The bacterial colony increased exponentially during these three days. For this study, this protocol was strictly reproduced on the cylinders described previously in this section by spraying one face (one cross-section) only. In order to be certain that the treatment was complete, the imbibition measurements presented in this work were done 40 days after the treatment. This curing time was selected as measurements done 40, 90 and 110 days after the treatment (SEM, microprobe, GIXD and imbibitions measurements) did not show any difference. The reader is referred to [18] and references therein for more details concerning the development of the process.

SEM micrographs for untreated tuffeau (Fig. 1a and b) showed sparitic and micritic calcite and spherolits of opal. After biotreatment (Fig. 2a and b) the surface was strongly modified and far less rough. Crusts covering the raw tuffeau generated a smoother surface with numerous cracks (Fig. 2b). These cracks were probably an artefact due to the high vacuum needed in the SEM chamber [18,19].

2.2. Imbibition measurements

Imbibition experiments are used to describe the transfer properties of a material via the imbibition coefficients [24,21,25,26]. The lower surface of the material is placed in contact with water and due to capillary forces, the water fills the pores, pushing the air inside the pores out of the sample. The water mass uptake and the height of the capillary front can be measured as a function of time. Neglecting the gravity effect on water and assuming cylindrical pores, the Washburn law predicts an evolution that is a function of the square root of time t for both the mass uptake Δm per surface area unit S and the capillary fringe height h:

$$\frac{\Delta m}{S} = A\sqrt{t} \tag{1}$$

$$h = B\sqrt{t} \tag{2}$$

where the imbibition coefficients A and B are defined as follows:

$$A = \pi r^2 \sqrt{\frac{r\gamma \cos\alpha}{2\eta}} \tag{3}$$

$$B = \sqrt{\frac{r\gamma \cos\alpha}{2\eta}} \tag{4}$$