

FROM LAB SCALE TO IN SITU APPLICATIONS _ THE ASCENT OF A BIOGENIC CARBONATE BASED SURFACE TREATMENT

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Abstract

Throughout the last decade, many authors have considered microbially induced carbonate precipitation as a promising technique to overcome shortcomings of conventional surface treatments. Despite high expectations and encouraging results from laboratory tests, biodeposition has hardly been applied in practice. So far, only one bacterial based treatment has been made commercially available. The rather low consolidation performance of this treatment together with its high product and labour costs may account for the limited spread of this technology. This paper presents our efforts to make the biodeposition treatment a highly performing and economically feasible technique and describes the parameters that affect the performance of the treatment. It summarizes the findings from several years of research indicating the advantages of a urea based pathway. By altering the product composition and application procedure we succeeded in optimizing the distribution of the biogenic crystals throughout the stone. The strengthening effect of the biodeposition treatment was evaluated by means of drilling resistance measurements and was compared to that of conventional surface treatments, both being applied under laboratory and in situ conditions. From this study, it is clear that our urea based biodeposition treatment performs well when applied in situ and can be offered at a reasonable price.

1 INTRODUCTION

Despite several decades of research on stone conservation, the quest for an effective CaCO_3 based surface treatment for calcareous stone remains ongoing. The application of such calcinogenic consolidants is considered to be a preferable conservation strategy, since they share physico-chemical affinity with the substrate to be treated.

Different strategies have been explored for the re-introduction of calcite into the pores of the stone, the lime-water treatment being one of the oldest and most well-known techniques. In the latter, formation of calcite is a result of the reaction of lime with atmospheric CO_2 . This technique has been applied to wall painting mortars and deteriorated calcareous stones in order to impart a slight water repellent and consolidating effect [1].

With the advent of nanotechnology in the last decade, there has been a revival in the use of lime as surface treatment for stone. The use of lime nanoparticles has been claimed to overcome the problems related to the use of traditional lime, i.e. poor solubility and fast sedimentation rate resulting in a high number of applications required [2]. Larson et al. [3] combined the use of calcite nanoparticles with lime in order to decrease the number of applications and drying time required with the lime water treatment. The strength obtained with these nanoparticles treatments, however, was limited to the outer surface.

Another technology that gained considerable attention in the last decade is the use of biologically induced precipitation of carbonate in building materials [4]. Biogenic crystals may form a protective layer on the surface and act as a cementing layer between the grains of the stone increasing its cohesion [5]. Despite many efforts by several research groups, so far only one biological treatment is commercially available. This so called Calcite Bioconcept treatment was already patented more than two decades ago [6].

Similar to the lime based treatments, most of the biodeposition treatments fail to meet the basic performance requirements of a consolidant. Because of their limited penetration depth they exhibit little or no improvement of the mechanical properties of the stone.

This paper summarizes our attempts to develop an efficient biogenic carbonate based surface treatment for limestone. Initial research was focused on the microbiological and chemical factors of the precipitation process. Amongst different enzymes (plant or microbial based) and metabolic pathways screened, the hydrolysis of urea with *B. sphaericus* appeared to be the most adequate treatment in a wide temperature range [7]. Contrary to other metabolic pathways [8], the hydrolysis of urea can be easily controlled and allows for the production of high concentrations of carbonate within a short amount of time. In a second stage, we directed our research efforts towards the problems most reported for inorganic consolidants, i.e. poor penetration abilities resulting in shallow and hard crusts and the formation of soluble salts as by-products [9].

Several parameters have been reported to influence the penetration depth of surface treatments [10]. In addition to examining the effect of climatologic conditions [7] and stone porosity [11], we have tried to optimize the penetration depth by altering the application procedure and the rate of carbonate deposition. Since transport of bacteria occurs in pores of which the diameter is at least two times that of bacteria [12], precipitation of carbonate at higher depths could be mainly observed for macroporous stone [11].

Our research indicated that the performance of the ureolytic biodeposition treatment was very dependent on the dosage of carbonate precursors [13] and the porosity of the stone [11], since both parameters affected the production and distribution of calcite crystals. As a

consequence, the consolidation of degraded and very porous stone would require substantial amounts of carbonate precursors, which would in its turn lead to the production of large amounts of by-products. In order to decrease the formation of soluble salts we proposed to replace a part of the carbonate precursors with nanoparticles. Our primary choice was the use of water-based CaCO_3 nanoparticles. Such particles, however, were not commercially available which required their in-house production [14]. Silica nanoparticles on the other hand, being water-based, commercially available and of interest for calcareous sandstone, were additionally investigated for their use as replacement of the carbonate precursors of the biodeposition treatment.

While a variety of durability parameters have been investigated, indicating the good protective performance of the biodeposition treatment (i.e. decreasing the uptake of water, and thereby, improving the resistance of the stone towards water-based degradation processes), this paper only reports on its consolidative effect, as evaluated by means of drilling resistance measurements.

2 MATERIALS AND METHODS

2.1 Limestone

Maastricht stone is a soft limestone with a total porosity up to 47% and a low compressive strength ($3\text{-}5 \text{ N.mm}^{-2}$). Its softness enables a clear evaluation of a strengthening effect. In this study, 2 types of stone specimens were used, i.e. cubes (10 cm) and prisms ($30 \times 30 \times 5 \text{ cm}^3$) for the surface treatments applied by pouring and spraying, respectively. Prior to the experiments, stones were dried at 80°C until constant weight (a weight change less than 0.1% between two measurements at 24 h intervals) was obtained. Then, all sides were covered with aluminium foil, except the one to be treated, to ensure that evaporation of water could only occur through the treated side. In case the treatments were applied by pouring, the foil was applied in such a way that it reached 2 cm above the surface that had to be treated. As such, loss of liquid during pouring was prevented.

2.2 Nanoparticles

Three types of nanoparticles were used in this study, i.e. calcium carbonate, calcium hydroxide and amorphous silica. Citrate-stabilized, water-based CaCO_3 nanoparticles (100-200 nm, 30 g.L^{-1}) were produced in-house according to the procedure described in [14]. Ethanol-based calcium carbonate (200-300 nm, 10 g.L^{-1}), ethanol-based calcium hydroxide nanoparticles (CaLoSil: 150 nm, 50 g.L^{-1} and CaLoSil Micro: 1-3 μm , 120 g.L^{-1}) and water-based silica nanoparticles (Dispercoll S3030: 9 nm, 400 g.L^{-1} and Dispercoll S5005: 55nm, 695 g.L^{-1}) were obtained from IBZ Salzchemie (Germany) and Bayer (Germany), respectively. All nanoparticles dispersions were applied to the stone in a dosage of 250 mL per cube, unless otherwise stated.

2.3 Biodeposition treatment procedure

Initially, all biodeposition treatments were applied in at least two steps, i.e. separate application of urease and carbonate precursors (i.e. urea and calcium salts). In a first series of experiments, biodeposition treatments were applied by pouring. The effects of the following parameters on the performance of the surface treatment were investigated: type and concentration of urease (microbial or plant based), type of calcium salt, concentration of

carbonate precursors, order of dosing urease and carbonate precursor solutions, dosage ratio of urea and carbonate precursor solutions, total dosage (L/m^2) and number of applications. Over 100 different treatments were evaluated. The most promising ones were selected for the second series of experiments, i.e. application by spraying.

In the second stage of our study, the urease and carbonate precursors were applied in a single step after modification of the composition of the urease medium. Because of commercial interest, the composition cannot be disclosed. The combined liquid was applied bottom-up by means of an Alta 2000 spray apparatus (Dimartino, Italy) from a distance of 30 cm from the surface. The dosage of liquid applied per spray application amounted to about $2.2 L/m^2$. In a final step, experiments were performed with industrially produced bacteria. Experiments were performed at $20\pm 2^\circ C$ and $65\pm 5\%$ relative humidity.

Additionally, several stones have been treated with the Calcite Bioconcept (CB) treatment to allow a clear comparison of the two types of biodeposition treatments. The CB treatment was applied under laboratory conditions at the Royal Institute for Cultural Heritage (Belgium) by J.F. Loubière (representative of CB). The stones were treated by immersion, capillary absorption (20 sec) or pouring (100 ml). A more detailed description of the CB treatment (oxidative deamination with *B. cereus*) can be found in [15].

2.4 Biodeposition combined with nanoparticles

Nanoparticles were applied to the stone by means of pouring or spraying, as described above. In a first series of experiments, biodeposition treatments were applied after stones treated with nanoparticles had obtained a constant weight (weight difference less than 0.1% over a 24 h interval when dried at room temperature). In a second series of experiments, nanoparticles were applied to the stone together with the urease source, followed later by the application of the carbonate precursors. The parameters investigated in this part of the study were the type and dosage of nanoparticles.

2.5 Conventional surface treatments

To gain a better insight into the efficiency of the bacterial treatments, results were compared to those obtained from conventional surface treatments. An ethyl silicate-based consolidant (KSE 300 HV) and a siloxane-based water repellent (Funcosil FC) were obtained from FTB-Remmers (Belgium).

2.6 Drilling resistance measurements

The strengthening effect was measured by means of the drilling resistance measurement system (DRMS Cordless SINT Technology, Italy). The system is equipped with a software program allowing the continuous recording and monitoring of the drilling resistance in relation to the advancement of the drill bit (\square 4.8 mm). For this study, a rotation speed of 600 rpm and a penetration speed of $40 \text{ mm}\cdot\text{min}^{-1}$ were used. The maximum penetration depth is about 3.5 cm. The results of the DRMS measurements are expressed as differential hardness profiles, obtained by subtracting the drilling forces measured after treatment from the reference values obtained on the corresponding untreated stone. For each type of treatment, 4 drilling measurements were carried out on each sample from which the average hardness profile was calculated.

3 RESULTS AND DISCUSSION

3.1 Consolidating effect of different types of nanoparticles

The strengthening effect of the nanoparticle treatment was clearly dependent on the type (carbonate or silica), the size and the dosage of nanoparticles used (Figure 1).

The highest strengthening could be observed for the silica nanoparticles (Figure 1C). Differences in diameter (9 vs. 55 nm) and viscosity (7 vs. 30 mPa.s) may account for the larger penetration depth of the 100 mL treatment with S3030 particles (± 25 mm) compared to the one with S5050 particles (± 13 mm). The larger particle size and density (1.39 vs 1.21 g.cm⁻³), on the other hand, are responsible for the higher strengthening obtained with the S5050 nanoparticles dispersion. With both types of silica nanoparticles, a significant and homogeneous strengthening could be observed up to 30 mm for the 250 mL treatment. The 250 mL treatment with S5050 particles exerted a higher consolidating effect compared to the ethyl silicate-based treatment. For both treatments, the increase in hardness can be attributed to the deposition of amorphous silica in the pores, the higher solids content of the S5005 treatment (i.e. 695 g/L) accounting for the higher strengthening compared to the ethyl silicate-based treatment (i.e. 300 g/L). While the primary function of the Funcosil treatment is to inhibit or decrease the uptake of water, the protective treatment also exerted a consolidating effect, although being limited to about 8 mm depth. Due to the deposition of large amounts of silica, resulting in an alteration of the porosity as observed from thin sections, stones treated with high dosages of nanoparticles were more prone to damage due to freezing and thawing.

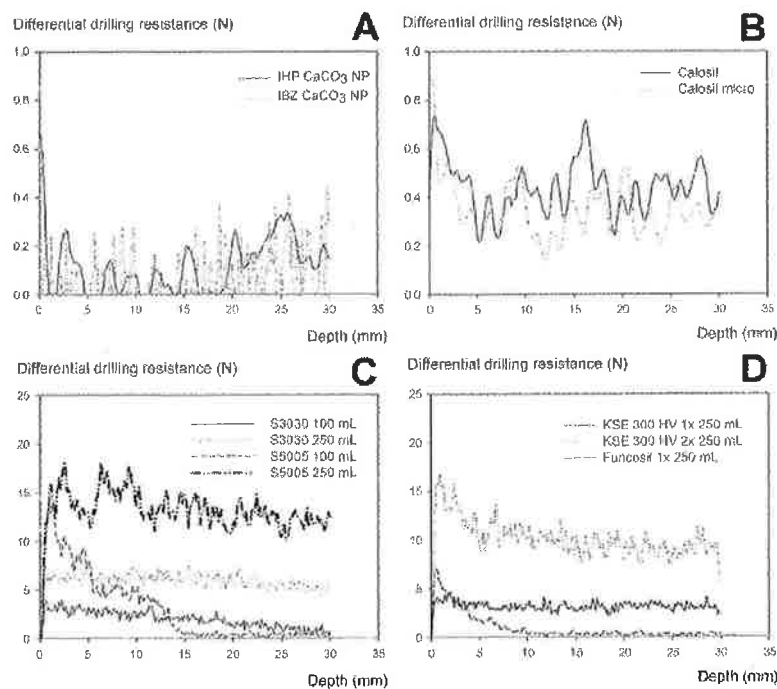


Figure 1: Strengthening effect of consolidation treatments with different types and amounts of nanoparticles (a: CaCO₃, b: Ca(OH)₂ and c: SiO₂) and of conventional surface treatments (d).

All treatments were applied by pouring.

The lowest strengthening was observed for the CaCO_3 nanoparticles (Figure 1A). The in-house produced (IHP) nanoparticles showed a tendency to aggregate which resulted in a poor penetration ability and in the formation of a white layer on the surface. The latter prevented the uptake of large volumes of nanoparticles dispersion. While the commercially available CaCO_3 dispersion exhibited a better stability, it was also unable to exert a noticeable consolidating effect (Figure 1A). Moreover, it also resulted in the deposition of a white carbonate layer on the surface of the stone.

The use of $\text{Ca}(\text{OH})_2$ nanoparticles resulted in a very limited strengthening (Figure 1B). The slightly better performance of the lime nanoparticles dispersions than that of the in-house produced carbonate nanoparticles could be attributed to the smaller particle size and higher density of the former.

3.2 Consolidating effect of different types of biodeposition treatments

While the strengthening effect of the Calcite Bioconcept treatment was very limited and restricted to the first 2 mm, a significant consolidation up to 30 mm could be observed with the Ghent University treatment (Figure 2). Contrary to earlier work, where the biodeposition treatment resulted in the formation of hard crusts or an inhomogeneous hardness profile ([14] and [15]), we succeeded in obtaining a homogeneous strengthening by modifying the application procedure and the composition of the bacteria and carbonate precursor medium.

The biodeposition treatment with nanoparticles exhibited a strengthening that was higher than that of the sum of the two separate treatments. The latter can probably be attributed to the fact that the silica gel affected the transport of the bacteria, and hence, the distribution of the carbonate cement throughout the stone, improving the connection between the stone grains. For the treatments applied by pouring, the biodeposition treatment (Figure 2) exhibited a much lower strengthening compared to that of the ethyl silicate-based consolidant (Figure 1).

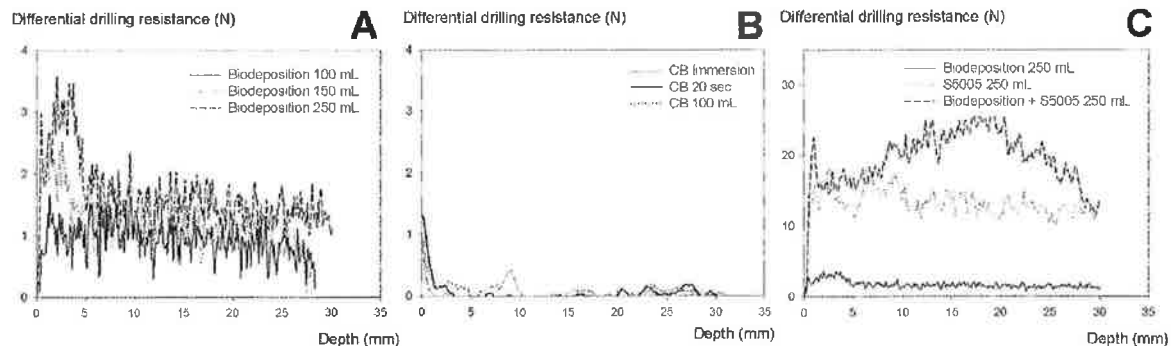


Figure 2: Comparison of the strengthening effect of the Ghent university biodeposition treatment (a), with that of Calcite Bioconcept treatment (b). Influence of the addition of silica nanoparticles on the strengthening effect of a biodeposition treatment (c).

3.3 Consolidating effect of spray-applied surface treatments

When applied by spraying, the biodeposition treatment exhibited a strengthening similar to that of the conventional ethyl silicate-based consolidant (Figure 3). Even a more homogeneous hardness profile was observed for the former, when only two spray applications had been performed. The smaller consolidation effect compared to the treatments applied by pouring can be largely attributed to the smaller dosage of product applied, i.e. about 1-3 times 2.2 L.m^{-2} compared to 1-2 times 25 L.m^{-2} .

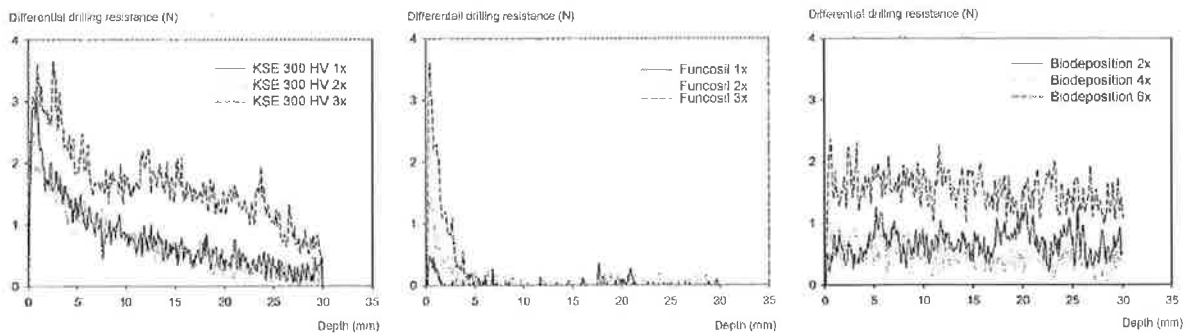


Figure 3: Comparison of the strengthening effect of the Ghent university biodeposition treatment, with that of conventional surface treatments. All treatments were applied by means of spraying.

4 CONCLUSIONS

By modifying the parameters that affect the penetration ability, we have succeeded to obtain a biogenic carbonate based surface treatment for stone that is cost-effective, able to homogeneously strengthen limestone up to depths of 30 mm and that has a similar or better performance than that of traditional surface treatments.

The replacement of carbonate precursors with silica nanoparticles presents a promising strategy to decrease the amount of by-products, but needs optimization prior to being used in practice. Because of more stringent regulations on the use of solvents, our water-based and compatible biodeposition treatment presents a valuable alternative to traditional solvent-based surface treatments. Moreover, our biodeposition treatment presents some advantages over the commercially available Calcite Bioconcept method. Whereas, the protective effect of the latter treatment is obtained after multiple spray applications over several days, our treatment entails both a significant protective and consolidating effect after two spray applications within the same day. The latter accounts for the lower cost of our treatment compared to that of the Calcite Bioconcept method. Furthermore, by optimizing the concentrations of the urease and carbonate precursor solutions, we were able to lower the cost of our treatment within the range of that of traditional consolidants.

To our knowledge, we are the first to offer a highly effective biodeposition treatment that combines the application of microorganisms and carbonate precursors in a single step methodology.

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