IMPACT OF BACTERIAL CARBONATE PRECIPITATION ON TRANSPORT PROCESSES IN CONCRETE

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Abstract

Surface treatments play an important role in the protection of construction materials from the ingress of water and other deleterious substances. Due to the negative side-effects of some of the conventional techniques, bacterial induced carbonate precipitation has been proposed as a novel and environmental friendly strategy for the protection of stone and mortar.

This paper reports the effects of bacterial carbonate precipitation on the water absorption of mortar specimens with different porosity. Durability was assessed from the permeation properties and resistance towards carbonation and chloride migration. The effectiveness of this treatment was compared to conventional surface treatments. The decrease in permeability due to the microbiologically induced deposition of a layer of calcium carbonate on the surface resulted in an increased resistance towards carbonation and chloride diffusion.

1. Introduction

Nowadays a broad array of products is available on the market for the protection of concrete surfaces [1-2]. Several of these products are organic coatings consisting of volatile compounds. The air-polluting effect of these compounds during manufacturing and coating works has lead to the development of new formulations such as inorganic coating materials. Traditional inorganic coatings consist of calcium-silicate compounds, which exhibit a composition similar to cement [3]. Promising results of an innovative technique based on microbial mineral precipitation have lead to several investigations concerning the use of bacteria in concrete. Microorganisms have been used to increase the compressive strength of cement mortar and for the remediation of cracks in concrete [4-6]. Our previous study has shown the potential of this technique as a possible tool to enhance the durability of concrete and mortar structures. The deposition of a layer of calcium carbonate on the surface of the mortar specimens resulted in a decrease of water absorption and permeability towards gas [7].

Microbial mineral precipitation involves various microorganisms, pathways and environments. Considerable research on carbonate precipitation by bacteria has been done by using ureolytic bacteria. These bacteria are able to influence the precipitation of calcium carbonate by the production of a urease enzyme. This enzyme catalyzes the hydrolysis of urea to CO_2 and ammonia, resulting in an increase of the pH and carbonate concentration in the bacterial environment [8]. Precipitation of calcium carbonate crystals occurs by heterogeneous nucleation on bacterial cell walls once supersaturation is achieved. The fact that hydrolysis of urea is a straightforward common microbial process and that a wide variety of microorganisms produce the urease enzyme makes it ideally suited for biotechnological applications [9].

Research has indicated that a concrete which is low in permeation properties lasts longer without exhibiting signs of distress and deterioration. Therefore, the permeation properties have been used principally for the comparison of the effectiveness of different surface treatments enhancing the durability of concrete [10]. The interrelationship between the different transport mechanisms and the deterioration mechanisms which occur in concrete has been widely investigated [11].

The goal of this research was to investigate the effects of bacterial carbonate precipitation on the transport processes in mortar and concrete in general. Water absorption was determined for mortar cubes of varying porosity (w/c). Furthermore, accelerated carbonation and chloride diffusion tests were performed. In order to gain a better insight into the efficiency of the bacterial treatments, results were compared to those obtained with conventional surface treatments.

2. Materials and methods

2.1. Mortar mixture proportions and dimensions of specimens

The mortar samples were made using an OPC (CEM I 52.5 N) content of 350 kg/m³, sand 0/4 content of 1050 kg/m³ and water-cement ratios of 0.5, 0.6 and 0.7. Average compressive strength of each mix was obtained from the measurements (according the Belgian standard NBN15-220) on three cubes (100 mm) after 28 days of water curing and amounted to 50.3 ± 3.96 MPa, 48.5 ± 3.40 MPa and 41.6 ± 3.91 MPa respectively. Cubes

(100 mm) were used for the accelerated carbonation tests. Cubes (40 mm) for capillary water suction experiments were cut from mortar slabs (900 x 600 x 40 mm). Cylindrical specimens were drilled out of mortar slabs (1200 x 700 x 50 mm) for chloride migration tests. For each mixture, a number of slabs were cast and cured for one day at 90 % R.H. and 20°C. The specimens were demolded after 24 h and then stored in water for 27 days prior to the drilling of the specimens. Afterwards the specimens were stored under humid atmosphere (60 % R.H., 20°C) until application of the surface treatment (at the age of 1-2 months).

2.2. Micro-organisms and growth conditions

Bacillus sphaericus LMG 225 57 (BCCM, Gent) was used for this study. Selection of this strain was based upon earlier work by our research group. This strain showed a high urease activity, a continuous formation of dense calcium carbonate crystals and a very negative ζ-potential [12,13]. Liquid culture media consisted of 3 g/L nutrient broth powder (Oxoid N.V., Drongen, Belgium), 2.12 g/L $NaHCO_3$ 10 g/L ammonium chloride and 10 g/L urea (VWR International, Leuven, Belgium). Liquid media were sterilized by autoclaving for 20 min. at 120°C. Cultures were incubated at 28°C on a shaker at 100 rpm for 24 h.

2.3. Treatment procedure

All treatments were applied on the side opposite to the troweled face.

The biodeposition treatment was applied as follows: Mortar specimens were immersed for 24 hours (15±5 mm depth) in a one day old stock culture of Bacillus sphaericus (ca. 10^7 cfu/mL). After this inoculation, specimens were wiped with a paper towel in order to remove some bacteria from the surface. In this way ureolytic activity primarily resulted from bacteria inside the specimens. Following this wiping, specimens were immersed in solutions of varying composition (culture media with 0 and 25 g/L calcium chloride) in order to investigate the effects of the external calcium source. In the absence of a calcium source plugging of the pores results from the presence of bacterial biomass and/or precipitation from calcium ions present in the pore solution. A lot of research on biodeposition was conducted with $CaCl_2$ as the calcium source [14-16]. The specimens were removed from the solution after 3 days.

Conventional surface treatments were applied with gentle brushing (following technical data instructions). Choice of treatments was based upon commercial availability and care was taken to cover a wide range of treatments acting according different mechanisms: coating (acrylates) and penetrating sealants (silanes, siloxane/alkoxysilane, sodium silicates).

2.4. Transport processes

2.4.1. Water absorption

To determine the increase in resistance towards water penetration a sorptivity test, based on the RILEM 25 PEM (II-6), was carried out. The mortar specimens (triplicate) were coated at the four edges adjacent to the treated side, to ensure unidirectional absorption through the treated side. The coating system comprises a single component silane-siloxane primer and a single component elastomeric coating based on an acrylic polymer.

After coating, the test cubes were dried at 45°C in a ventilated oven, establishing a mass equilibrium of less than 0.1% between two measurements at 24 hour intervals, to ensure low uniform moisture content in the matrix. The specimens were then exposed, to 10±1 mm of water, with the treated side facing downwards (water level about 2 mm above the base of the specimen). This was done in an atmosphere of 20°C and relative humidity of 60%. The water level was kept constant through addition of tap water. At regular time intervals (15, 30 min; 1, 1.5, 3, 5, 8, 24, 72, 96, 120, 144 and 168 h) the specimens were removed from the water and weighed, after drying the surface with a wet towel. Immediately after the measurement the test specimens were submerged again. Results of capillary water suction are expressed as the relative capillary absorption index as proposed by [17]:

$$I_{Cr} = \frac{\int_{t_0}^{t_f} f(Q_e).dt}{\int_{t_0}^{t_f} f(Q_R).dt} \qquad (1)$$

Where the numerator is the amount of water absorbed during the testing by the examined sample (mg/cm² $s^{1/2}$); and the denominator is the amount of water absorbed during the testing by the reference sample (mg/cm² $s^{1/2}$). A value below 1 indicates a relative decrease of water absorption, a value above 1, a relative increase.

2.5. Degradation processes

2.5.1. Accelerated carbonation test

The accelerated carbonation tests were performed in a CO_2-closet under a temperature of 20±3 °C, a relative humidity of 70±10 % and a concentration of CO_2 of 10 %. Before the test, the mortar cubes were dried at 60°C establishing a mass equilibrium of less than 0.1% between two measurements at 24 hour intervals. The following day the surface treatment was applied on the side opposite to the troweled face. The remaining sides were coated in order to prevent the penetration of CO_2. The coating system comprises a single component silane-siloxane primer and a single component elastomeric coating based on an acrylic polymer. The specimens were stored in an atmosphere of 20°C and relative humidity of 60% for 7 days prior to start of the accelerated carbonation. After two weeks of carbonation, specimens were removed from the closet. A slice (10 mm) perpendicular to the treated surface was cut off and sprayed with phenolphthalein solution for the determination of the carbonation depth. The remaining mortar specimen was coated again with the silane-siloxane primer and acrylic coating and put back in the CO_2-closet. Carbonation depth was determined after 2, 4 and 6 weeks. Resistance towards carbonation is expressed as the carbonation rate constant (K). This parameter can be obtained as follows:

$$x = K.\sqrt{t} \qquad (2)$$

where x is the mean carbonation depth [cm] after a certain time [years] [18].

2.6. Accelerated chloride migration coefficient

The resistance towards chloride diffusion was investigated by means of the CTH rapid test according to the NT Build 492 Nordtest method. In brief, an external electrical potential was applied axially across the specimen. This forced the chloride ions outside to migrate into the specimen. After a certain test duration the specimen was axially split and a silver nitrate solution was sprayed on the freshly split sections. The chloride migration penetration depth was measured from the visible white silver chloride precipitation. Results are expressed as the non-steady-state migration coefficient. This parameter is obtained as follows:

$$D_{nssm} = \frac{0.0239.(273+T).L}{(U-2).T}.\left(x_d - 0.0238.\sqrt{\frac{(273+T).L.x_d}{U-2}}\right) \qquad (3)$$

where D_{nssm} is the non-steady-state migration coefficient [m²/s], U is the absolute value of applied voltage [V], T is the average value of the initial and final temperatures in the anolyte solution [K], L is the thickness of the specimen [m] and x_d is the average value of the penetration depth [m].[18, 19]

2.7. Statistical analysis

Experiments were performed in triplicate. Error bars on graphs show the standard error. Prior to comparison of mean values with one-way anova, univariate analysis was performed in order to determine the influence of each specimen on the global result of each treatment. Statistical Software SPSS 12.0 was used for this purpose. Grouping of treatments based on significant differences in mean values was done according Student Newman Keuls or Dunnet T3 tests, depending on homoscedasticity results of the Levene test.

3. Results

3.1. Transport processes

3.1.1. Water absorption

Figure 1 summarizes the effects of the water-cement ratio and the surface treatment on the water absorption of the mortar specimens. With exception of the silicones, all treatments resulted in a IC_r value below 1 indicating a relative decrease of water absorption compared to the untreated samples. The influence of the water-cement ratio on the capillary water uptake was most pronounced for untreated mortar specimens and specimens treated with bacteria. The water absorption increased with increasing water-cement ratio for these cubes. The presence of bacteria resulted in a significant decrease of the water uptake compared to untreated specimens. When a calcium source was added to the medium an additional significant decrease of the water absorption coefficient was noticed. Acrylates, silanes or silanes/siloxanes decreased the water absorption of mortar specimens by about 90% for all the water-cement ratios. With exception of the most porous specimens (w/c 0.7) similar results were obtained for the biodeposition treatment in the presence of calcium chloride. Results from the latter treatment were comparable to those of the specimens on which silicates were applied.

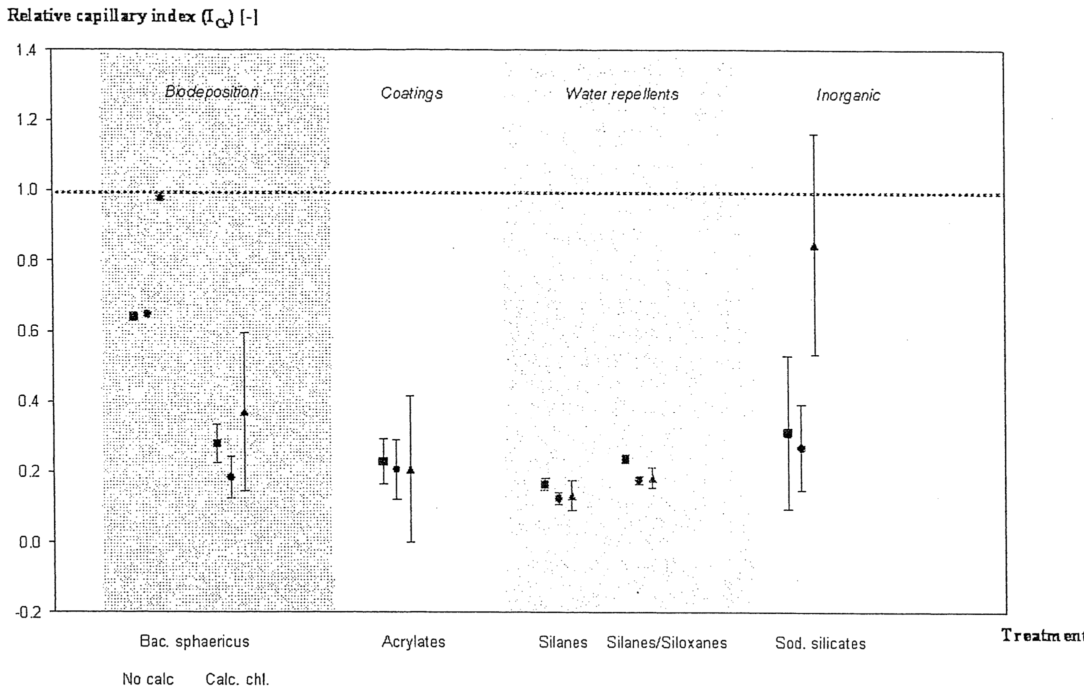

Figure 1: Capillary water suction results expressed as the relative capillary index (ICr) for different grades of mortar (w/c 0.5: ■, w/c 0.6: ● and w/c 0.7: ▲) applied with different types of surface treatments. A value below 1 (dashed line) indicates a relative decrease of water absorption

4. Degradation processes

4.1. Carbonation

The effects of the water-cement ratio and the surface treatment on the resistance of mortar cubes towards carbonation are summarized in Figure 2. The value of the carbonation rate constant increased with increasing water-cement ratio. Significant differences in carbonation depth between treated and untreated specimens were already noticeable after 2 weeks of accelerated carbonation (results not shown). The addition of bacterial biomass resulted in a significant smaller carbonation rate compared to untreated cubes. The effect of this addition increased with increasing w/c, resulting in a decrease of K about 24 %, 30 % and 37% respectively. The combination of the biomass and a calcium source (biodeposition) resulted in an additional significant drop of the carbonation rate. Except for the most porous specimens (w/c 0.7) the increased resistance towards carbonation of cubes treated with biodeposition was similar to that of the acrylic coating. The presence of the water repellent silanes and siloxanes had no protective effect towards carbonation.

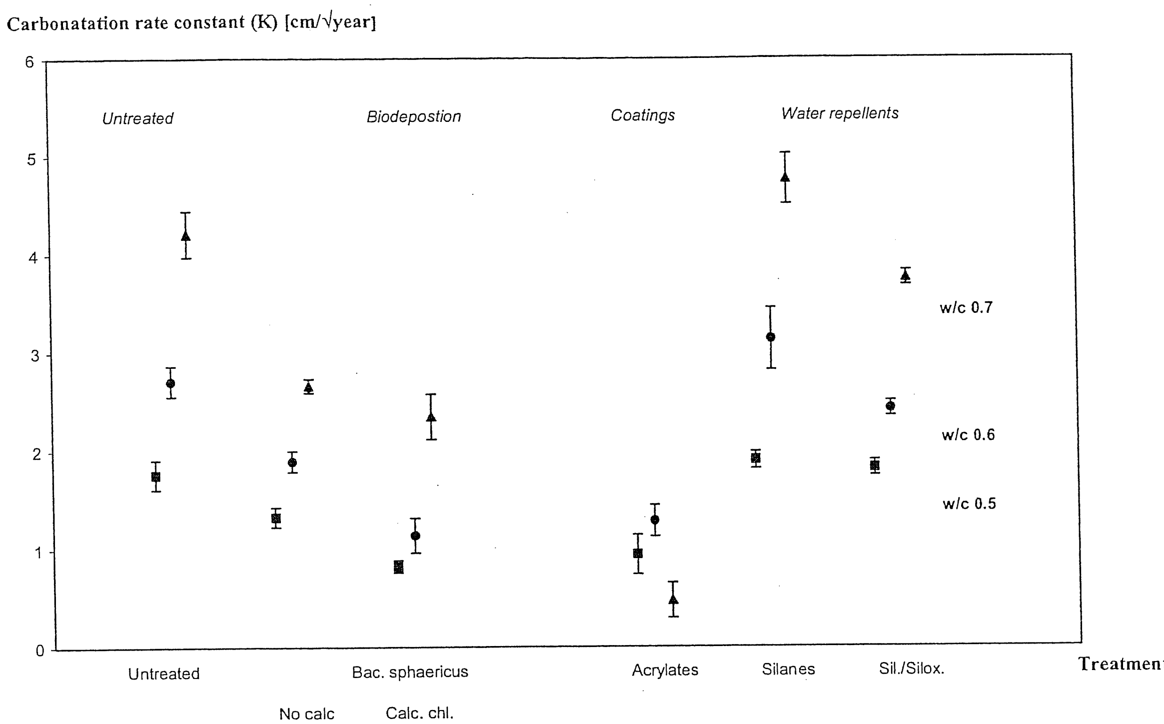

Figure 2: Carbonation rate constants, K, for different grades of mortar (w/c 0.5: ■, w/c 0.6: ● and w/c 0.7: ▲) applied with different types of surface treatments

4.2. Chloride migration coefficient

The resistance of mortar specimens towards the diffusion of chlorides expressed as the chloride migration coefficient is shown in Figure 3. For untreated specimens the value of this coefficient increased with increasing water-cement ratio. With exception of the biomass treatment, all treatments resulted in an increased reduction of D_{nssm} with increasing w/c. The addition of bacterial biomass resulted in an increased resistance towards the penetration of chlorides compared to untreated cubes. The results were most pronounced for the less porous specimens (w/c 0.5), which obtained a 25 % decrease of the chloride migration coefficient. In the case of the more porous specimens, the differences however were not significant. The combination of the biomass and a calcium source (biodeposition) resulted in significant lower chloride migration coefficients compared to untreated specimens. The increased resistance towards the migration of chlorides of cubes treated with biodeposition was similar to that of the acrylic coating and the water repellent silanes and larger than in the case of the silanes/siloxanes mixture.

5. Discussion

The current study demonstrated that the biodeposition treatment resulted in an increased resistance of mortar specimens towards degradation processes. The results from this research tend to confirm the interrelationship that exists between transport and degradation mechanisms occurring in concrete.

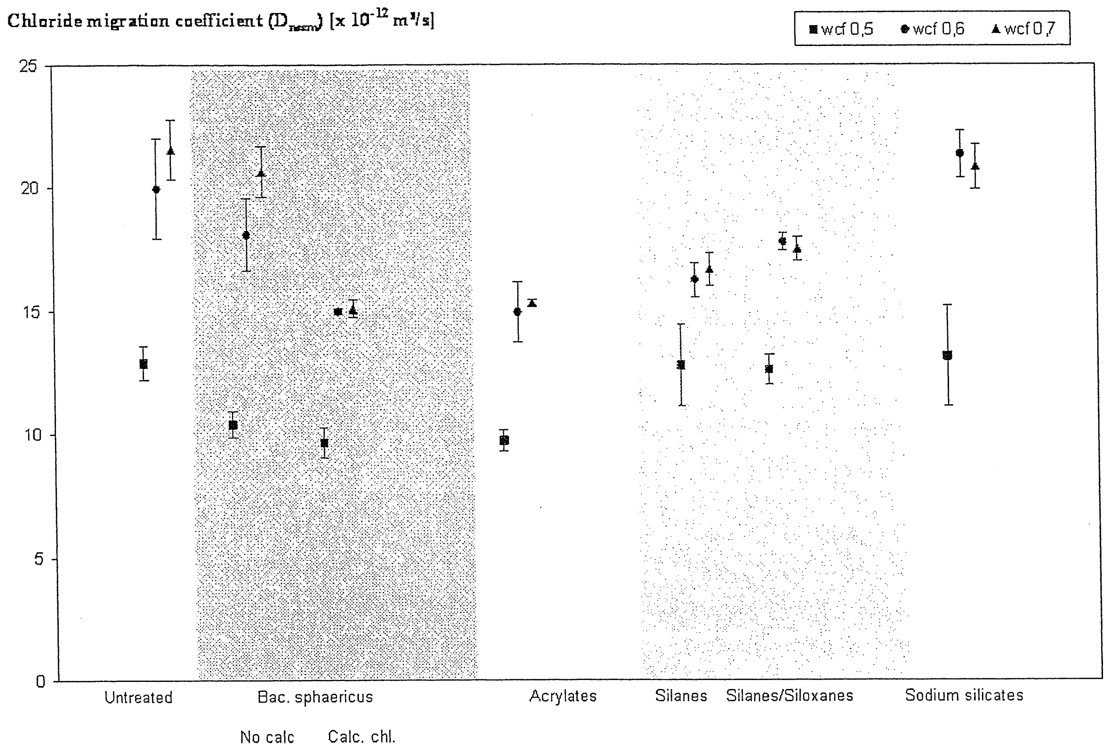

Figure 3: Chloride migration coefficients, D_{nssm}, for different grades of mortar (w/c 0.5: ■, w/c 0.6: ● and w/c 0.7: ▲) applied with different types of surface treatments.

The deposition of a layer of calcium carbonate on the surface results in a decrease of the permeation properties of mortar specimens. Plugging of the pores as a result of the presence of calcium carbonate crystals and biomass, accounts for the decreased water absorption.As a result of the biodeposition treatment, specimens with a w/c 0.6 showed significantly less water absorption than untreated specimens with a w/c 0.5. Specimens with w/c 0.7 on which the biodeposition treatment was applied however showed a slightly higher water absorption coefficient than the latter. Conventional surface coatings showed similar water absorption regardless the water-cement ratio. The higher water absorption coefficient of the most porous specimens applied with the biodeposition treatment could be due to an incomplete coating. Repeated application of bacteria and a calcium source could result in an additional decrease of the water absorption. Nemati and Voordouw noticed an additional decrease of the permeability of sandstone cores after injecting $CaCO_3$ forming reactants for a second time [20]. The influence of repeated applications of bacteria and a calcium source on the permeation properties of concrete will be investigated in future research.

The biodeposition treatment resulted in an increased resistance towards carbonation. The rate of carbonation and the performance of the surface treatment were correlated to the water-cement ratio. Several authors have demonstrated an increase in the carbonation rate in concrete with increasing water-cement ratio. Carbonation was shown to be related to the nature of the pores, with larger pores giving rise to higher carbonation depths [19]. Basheer *et al.* reported that for film forming coatings and sealants in order to be effective against carbonation, the thickness of the treatment should be at least 200 μm [1]. Preliminary observations from SEM and μCT analyses indicated that the thickness of the calcite layer is at least between 50 and 100 µm. The aim of current investigations is to determine the depth of penetration and the thickness of the calcium carbonate layer.

Cubes treated with the biodeposition method showed a similar resistance towards carbonation as those treated with the acrylic coating. Several authors have reported on the effectiveness of acrylic coatings as anti carbonation treatment [1]. According to these authors alkyl-alkoxy silanes do not improve the resistance of concrete towards carbonation. Siloxanes with large alkyl groups however may marginally reduce the carbon dioxide diffusion. The carbonation rate constants measured in the accelerated tests are considerably higher than those measured in atmospheric conditions due to the higher CO_2 content of the air and the preconditioning of the specimens prior to the test. Nevertheless they give an indication of the difference in resistance between surface treated and untreated concrete towards carbonation under similar conditions. Future research however will investigate the effect of the submersion of the cubes in the bacterial suspension and nutrient medium on the moisture content of the surface layer as this parameter has an influence on the gas diffusivity [21].

The presence of the biodeposition treatment improved the resistance towards chloride penetration. The increased resistance towards the migration of chlorides of specimens treated with bacteria and a calcium source was similar to the coatings and water repellents under investigation. Published work on the chloride resistance of surface treated concrete is mainly based on the results of diffusion tests [1, 22]. The long duration of this method however has encouraged some researchers to investigate the use of more rapid tests [2, 23]. Ibrahim *et al.* investigated the effectiveness of different surface treatments with imposed current testing and corrosion potentials and current density measurements. They found that silane/siloxane with top coat, silane and acrylic coating were very effective in decreasing the rate of reinforcement corrosion. According to these authors sodium silicate, silicone resin solution and silane/siloxane were not effective in delaying the initiation of reinforcement corrosion [2]. Basheer *et al.* reported on the performance of different surface treatments towards chloride penetration. They state in their review that the best performance is obtained with silanes. A two coat system consisting of a silane primer and a acrylic top coat also exhibited superb performance [1]. The results of our research are in agreement with these findings.

One of the factors to be considered in coating selection is the durability of the coating. As calcium carbonate is solubilised in acidic environments, there is a need to investigate the effect of acidic rain on the durability of the biodeposition treatment. Bacterially induced calcite crystals however, are assumed to be more resistant to dissolution since it has been experimentally demonstrated that biologically deposited calcite is less soluble than inorganically precipitated calcite [24]. In future research the durability of the calcite layer under varying conditions will be investigated.

6. Conclusion

Biodeposition has the potential to improve the durability of concrete structures. The transport mechanisms in concrete are influenced by the surface treatment with the ureolytic bacteria and a calcium salt. The presence of a layer of calcium carbonate and biomass results in a decrease in water absorption. The results from the accelerated carbonation and chloride migration tests confirm the interrelationship between concrete durability and transport processes. The presence of a layer of calcite delays the progress of carbonation respectively chloride penetration. Best results were obtained with the combination of Bacillus sphaericus and calcium chloride, with which a similar protection as some of the conventional surface treatments was obtained.Further research however is needed to investigate the impregnation depth and the durability of the treatment under environmental conditions.

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