

Effect of ethyl silicate on salt crystallization resistance of Maastricht limestone

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Abstract

Consolidant treatments aim to re-establish the cohesion in decayed materials showing decay patterns as sanding or powdering. Ethyl silicate (TEOS) is the most used type of consolidant for inorganic porous materials in the last 30 years. This product, which works through precipitation of silica gel in the pores of the material, is known to have a good chemical compatibility with siliceous substrates (sandstone and brick), but much less with lime based materials as limestone and mortar. In order to encounter this shortcoming, in the last years, research has been focused on the modification of ethyl silicate products to make them more compatible with lime-based substrates.

In this study the effect of an ethyl silicate product, commercialized for application on limestone, has been investigated. The research concerned more specifically the resistance of Maastricht limestone with respect to salt crystallization. The penetration depth and the strengthening effect of the treatment have been assessed, using respectively dithizone and the Drilling Resistance Measurement Method (DRMS). Further the influence of the treatment on water absorption and drying, measured by standard test procedures, has been assessed. An accelerated salt crystallization test has been carried out to assess the effect of the treatment on the salt resistance of the Maastricht limestone. All tests have been performed on fresh stone as well as on artificial analogues for decayed stone, obtained by re-aggregating the original stone following a method developed by the authors.

The results showed that the studied ethyl silicate product is able to reach a very good penetration depth in the Maastricht limestone and to confer a significant strengthening to the substrate, without significantly altering the overall drying behavior of the material. However, a not homogenous distribution of the product and of its strengthening effect in the impregnated zone has been measured. This has, for the salt crystallization test on specimens with the re-aggregated layer, caused salt accumulation behind the outer zone, enriched in ethyl silicate, which consequently resulted in the detachment of this 2-3 mm thick layer.

The differences in extent and type of damage observed during the crystallization test between fresh stone and re-aggregated stone specimens underline the necessity to test consolidant products on (artificially) decayed and not on fresh substrates in order to obtain reliable results.

Keywords: Maastricht limestone, ethyl silicate, salt crystallization test, analogues for decayed stone.

1 Introduction

Consolidant treatment can be defined as the impregnation with a product that, penetrating in depth in a material, improves the cohesion of the decayed part and possibly the adhesion of this to the sound material beneath. The expected result is a better resistance of the consolidated material to decay phenomena.

Amongst organic consolidants, products based on ethyl silicate (TEOS; tetra-ethylorthosilicate) are the most commonly used in the last decades. The chemical reaction leading to consolidation can be summarized as follows: in contact with water, present in the stone, the ethyl silicate breaks down into ethyl alcohol (which evaporates) and silicic acid. The latter forms a silica gel, that is deposited in the pores and the fissures of the materials, thus re-establishing cohesion. As silica is the main component of ethyl silicate, this consolidant is particularly suitable for materials containing silica, as sandstone and brick. However, because of the lack of effective alternatives, ethyl silicate is also often used for consolidation of lime-based mortar and limestone. In the last years different solutions for this problem have been looked for, including pre-treatment of the lime-based material in order to improve the adhesion of TEOS to the substrate [1], and modification of TEOS for improvement of its compatibility with lime-based substrates. [2, 3] In this research, a commercial ethyl silicate product, on purpose modified to increase its compatibility with lime-based substrates, has been tested.

Especially when assessing the feasibility of a consolidant product for application on substrates with a heritage value, the fulfilment of requirements related to its compatibility with the substrate should be considered [e.g. 4-7]. A treatment can be defined as compatible if it does not cause or enhance any damage (technical or esthetical) to the historic material. Damage processes such as salt crystallization should therefore not be enhanced by the consolidation. This might occur if the treatment significantly modifies the properties of a material: for example, a decrease in the evaporation rate due to the presence of the consolidant, may lead to salt accumulation behind the treated layer, with possible subsequent spalling of the last.

Moreover, as a consolidant aims at re-establishing the cohesion and increasing the strength of a decayed substrate, an effective consolidation is expected to improve the resistance of a material with respect to damage processes as e.g. salt crystallization. The effect of a consolidation on the salt crystallization resistance of a material can be assessed by an accelerated crystallization test comparing the behavior of treated and untreated specimens.

An important limitation, when testing the effect of a consolidant, is given by the difficulty of applying the product on a sufficient number of representative, weathered specimens. In laboratory tests, consolidants are usually applied on sound, fresh materials, which might invalidate the obtained results or complicate their interpretation. This choice is due to the difficulty of finding representative, reproducibly decayed substrates for testing. These might be either sampled from the field or produced in the laboratory. The first option is seldom applicable in the field of conservation: it is in fact generally not desirable nor allowed to sample a sufficient amount of materials from monumental buildings and/or objects. Moreover, differences in properties (as e.g. salt content, strength) among the specimens might be present.

In this research, reproducibly weathered specimens, obtained by a novel method developed by the authors, have been used [8].

2 Materials and methods

2.1 Stone type and properties

This research has been carried out on Maastricht limestone, a stone widely used for building purposes in the southern part of The Netherlands and in adjacent Belgium [9]. The Maastricht limestone is a very soft, yellow coloured and highly porous limestone composed by calcium carbonate bioclasts of about 300-500 μm diameter, poorly cemented by sparite. Its open porosity (51 vol%) is very high and constituted by coarse pores in the range of 40 μm [8]. Its CaCO_3 content is very high, up to 94-

98 wt.% [9]. Weathering often manifests in Maastricht limestone as loss of cohesion and powdering of the surface (figure 1).



Figure 1: Loss of cohesion and powdering of Maastricht limestone (castle ruine, Valkenburg, The Netherlands)

2.2 Specimens

Two types of specimens have been used in this research:

- Cylinders of fresh Maastricht limestone of 45 mm diameter and 50 mm height
- Cylinders of 45 mm diameter consisting of a core of 40 mm height fresh Maastricht limestone with a 10 mm re-aggregated layer on top (figure 2).

The cylinders of fresh stone were drilled out of slabs, with the natural layering of the stone perpendicular to the surface of the cores. This choice was made to reproduce the practice situation, where stone blocks are generally laid with the natural layering perpendicular to the surface.

The re-aggregated layer reproduces a decayed surface and it has been made following a procedure developed by the authors. This procedure, described in detail in [8], consists in grinding the limestone, sieving the

obtained particles in an appropriate grain size range and re-aggregating them by the use of an air lime binder in suitable proportions. The obtained “mortar” is then applied as a layer on the sound material and allowed to carbonate. The final result is a reproducible substrate, having a similar chemical composition as the original material but an increased open porosity and main pore size. These characteristics are representative for a decayed material [10]. The open porosity and pore size distribution of fresh and re-aggregated Maastricht limestone are compared in figure 3: the open porosity of the re-aggregated layer is 54%, with mostly pores in the range of 80 μm . As expected for a decayed material, the open porosity and the main pore size of the re-aggregated layer are larger than those of the fresh stone. Figure 4 shows a thin section of the re-aggregated layer on the fresh stone illustrating the higher and coarser porosity of the re-aggregated part with respect to the original stone. A zone slightly enriched in binder is visible at the interface between re-aggregated and fresh stone.

All specimens were coated on the cylindrical side with a two component epoxy resin in order to avoid absorption of the treatment (during the application) and water (during the water absorption and the salt crystallization tests) from this side.

Next to the small specimens described above, 15 x 15 x 10 cm specimens of fresh stone and of stone with re-aggregated layers were prepared to be used for assessing the penetration depth of TEOS.



Figure 2: Specimen of Maastricht limestone with re-aggregated layer on top

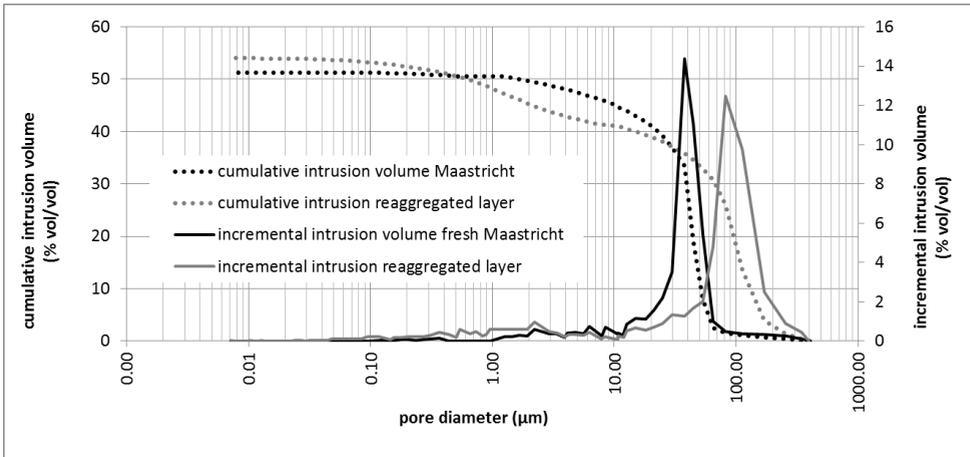


Figure 3: Open porosity and pore size distribution of the fresh Maastricht limestone and of the re-aggregated layer.

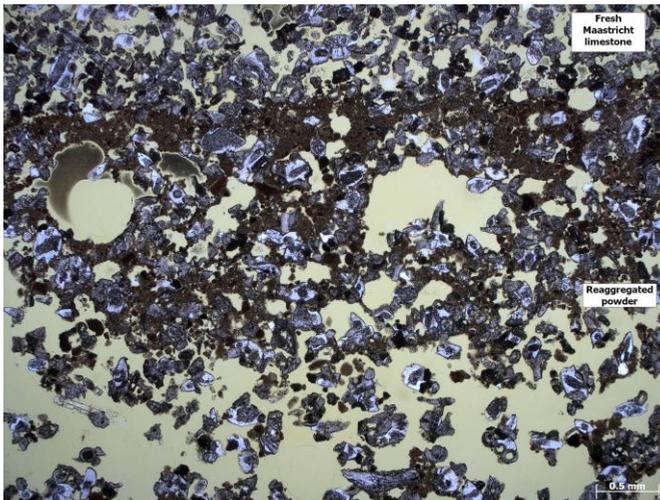


Figure 4: Plane polarized microphotograph of re-aggregated layer (below) on fresh Maastricht limestone (above) (original size: 5.4 x 3.5mm)

2.3 Application of the consolidant

The selected consolidant is a commercial product based on ethyl silicate. According to the information from the producer, this product has improved adhesion properties and it is especially suitable for application on

limestone substrates. According to the producer's technical sheet, the percentage of active components in the product is 95%, leading to about 30% gel formation after reaction.

Both specimens of fresh stone and specimens with re-aggregated layer were treated. The specimens were conditioned 20 °C 50% RH before treatment. The product was applied by brush on the surface, in two applications at a distance of one day. In order to define the amount of product to be used, some trial applications were carried out: in the trials, the treatment was applied until a penetration depth of 10 mm (assessed visually) was reached; this penetration depth corresponds to the thickness of the re-aggregated layer. The average amount of product absorbed was then calculated and the specimens were treated with this amount of product. The average consumption was slightly higher for specimens with re-aggregated layer than for those of fresh stone: 8.4 l/m² and 8 l/m², respectively. The high consumption is due to the very high absorption typical for this type of limestone.

After treatment, the specimens were cured at 20°C, 50% RH for at least three weeks before the start of the tests.

2.4 Penetration depth

Different methods exist to check the penetration depth of consolidant products. Some of these only assess the penetration of the product (as for example by the use of an indicator or microscopy observations), while other methods assess the extent and depth of its consolidating effect. In this research the depth of impregnation has been indicatively evaluated by spraying a solution of dithizone (diphenylthiocarbazone) in acetone on a cross section of some treated specimens few weeks after the treatment: a change in color from green to pink/orange indicates the presence of the product. The principle at the base of this colour change is the reaction of dithizone with metallic elements, often present in the catalyzing agents of ethyl silicate products [11]. Additionally, scanning electron microscopy, equipped with Energy Dispersive X-ray Spectroscopy (SEM-EDS) (FEI NovaNanoSEM650) has been used to investigate the distribution of the product in the porous system of the stone.

Moreover, the extent and depth of its consolidating effect have been measured by means of the Drilling Resistance Measurement Method (DRMS) by Sint Technology. This instrument can assess the consolidating effect by measuring the resistance the substrate opposes to the penetration of a drill; both the rotation speed and the penetration speed of the drill are constant and can be adjusted depending on the strength of the stone [12].

In this research, DRMS measurements have been carried out on fresh Maastricht limestone and on re-aggregated substrates, before and after treatment. Measurements were carried out up to 30 mm depth. A rotation speed of 40 rotations per minute and a penetration speed of 40 mm per

minute were used. 10 DRMS profiles were drilled for each specimen from which the average was calculated. For an optimal consolidation, the strength of the decayed and consolidated material should be equal to that of the sound stone.

2.5 Water absorption and drying test

The effect of the treatment on the absorption and drying behavior was determined, both on specimens with re-aggregated layer and on fresh stone specimens. The water absorption was determined and the water absorption coefficient (WAC) calculated, according to the CEN standard EN 1925-1999. In order to minimize the variance between the specimens, the absorption and drying were measured on the same specimens before and after treatment. Besides, the drying was assessed on the same specimens on which water absorption had been measured. Absorption and drying were measured in a climatic chamber at 20 °C, 50% RH. All experiments were carried out in threefold.

2.6 Salt crystallization test

The effect of the consolidant on the salt resistance of the stone to NaCl and Na₂SO₄ crystallization was assessed on specimens with a re-aggregated layer on top (treated and untreated) and on fresh stone specimen (treated). The crystallization experiment was carried out in threefold.

The accelerated salt crystallization test was carried out according to an adapted version of the procedure developed in the EC projects SCOST [13] and COMPASS [14].

The procedure used in this research includes the following steps:

1. The specimens are contaminated with NaCl and Na₂SO₄ solutions. The amount of solution is equal to the capillary water content, i.e. to the amount of solution necessary to wet the upper surface of the specimen when its bottom surface is in contact with the solution. In this way it is ensured that the salt solution reaches the upper (treated) surface of the specimen. The concentration of the salt solutions (10% and 5% for NaCl and Na₂SO₄, respectively) is calculated in such a way as to obtain a salt content in the specimens of 3 and 1.5% by weight, for NaCl and Na₂SO₄, respectively. The different salt concentrations were chosen because of their different damaging effect. Higher Na₂SO₄ concentrations might result in immediate damage in all the tested specimens, making a comparison impossible; a lower NaCl concentration might be insufficient to cause damage within the test period.

2. The specimens are dried. The drying includes two periods:
 - a. a first period, in which the specimens are dried at temperature and RH conditions cycling between 20°C, 65% RH (8 hours) and 40°C, 20% RH (16 hours), until 80% of the absorbed water is evaporated;
 - b. a second period, in which the RH crosses the RH of equilibrium of the salts, in order to stimulate hygroscopic moisture uptake and release and thus dissolution/crystallization cycles. Two cycles of 20°C, 96% RH and 60°C, 0% RH for a total period of one week are foreseen.
3. The appearance of efflorescence and the occurrence of damage are described and photographically recorded. The specimens are brushed and the material loss (salt + debris) measured. The debris is then separated from the salt, by dissolving the salt and filtrating the aqueous solution.
4. The specimens are re-wetted with an amount of demineralized water equal to the amount of salt solution used at the start
5. Steps 2-4 are repeated 4 additional times.

3 Results

3.1 Penetration depth

The test with dithizone, carried out on specimens of fresh and re-aggregated stone specimens, showed a very deep penetration of the consolidant, which reached more than 30 mm in both fresh and re-aggregated stone (figure 5).

The SEM-EDS observations confirmed the presence of the consolidant in the depth of the stone. The product is present in a large amount in the re-aggregated layer, where it can be easily distinguished because of the presence of shrinkage cracks, a typical feature of hardened ethyl silicate (figure 6).



Figure 5: Penetration depth of ethyl silicate in a specimen with re-aggregated top layer (the pink-orange colour indicates the presence of the treatment)

The DRMS profiles of sound Maastricht stone before and after treatment are reported in figure 7. The results show that the 'hardness' of the stone has increased after treatment up to the whole measured depth (30 mm); this means that the impregnation depth is at least 30 mm, and confirms the results of the dithizone test and of the SEM observations. The very deep impregnation depth (deeper than the 10 mm desired) is due to the strong capillary suction / absorption of this stone as a result of the coarse pore structure of the Maastricht limestone. Further, due to the fact that the application was carried out on a horizontal surface, gravity might also have played a role to the transport of the consolidant to this depth. The profile of the consolidated stone shows a higher hardness at the surface, indicating that an accumulation of the strengthening product occurred in the outer 3-4 mm. This may have consequences for moisture and salt transport.

The DRMS measurements on the fresh stone, before and after treatment, allow to assess the strengthening effect of the treatment; however, it is difficult, only on the basis of these results, to evaluate whether consolidation is suitable or excessive. An objective evaluation can be better obtained by comparing the strength of the sound stone with that of the decayed layer after consolidation: for an optimal consolidation, the strength of the decayed and consolidated material should be equal to that of the sound stone. Besides, in any case the strength of the consolidated layer should not be higher than that of the sound stone.

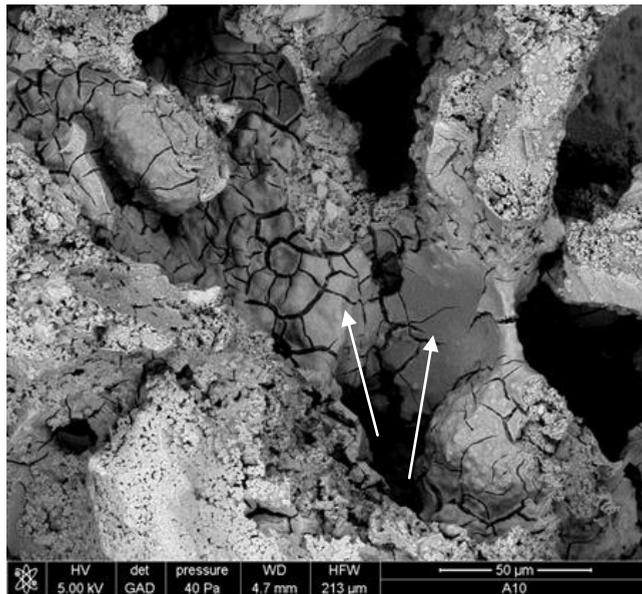


Figure 6: SEM microphotograph of the re-aggregated top layer of a specimen treated with ethyl silicate. The arrows indicate the product bridging stone particles.

In figure 8, the DRMS profiles of specimens with re-aggregated layer, before and after consolidation, are reported. After treatment, there is an overall increase of the strength up to 30 mm depth in the stone, but the strengthening effect is not as homogenous as desired. Peaks in the DRMS profile are visible at the surface (as observed in the untreated specimen) and at the interface between the re-aggregated layer and the fresh stone underneath (probably due to the abrupt change in pore size distribution and to the presence of a slightly denser layer at the interface). At both these locations, the strength of the consolidated re-aggregated layer is much higher than that of the sound (fresh) stone. This constitutes an undesired effect, which may have consequences for the durability of the consolidated material: because of the differences in strength, decay phenomena as scaling and/or spalling may occur.

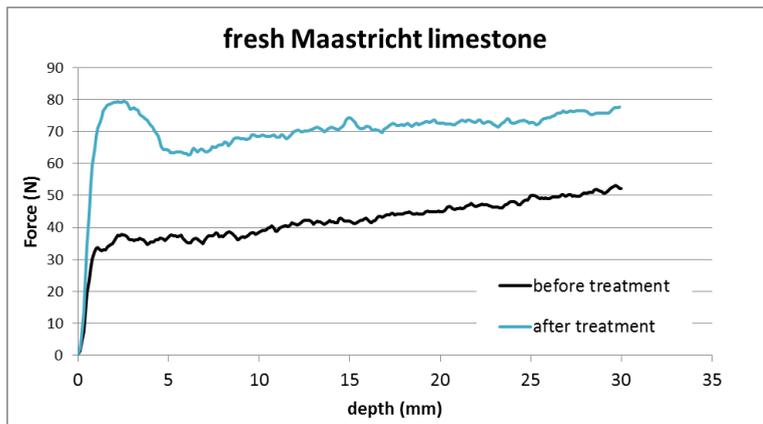


Figure 7: DRMS profile of sound Maastricht limestone before and after treatment (each profile is the average of 10 measurements).

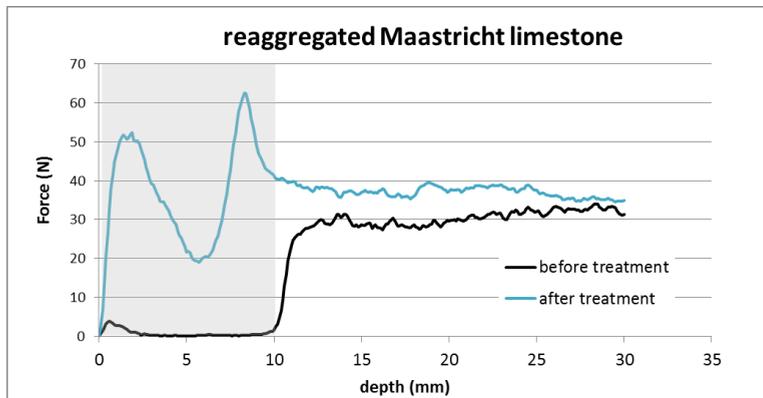


Figure 8: DRMS profile of re-aggregated Maastricht limestone before and after treatment; the grey area indicates the thickness of the re-aggregated layer (each profile is the average of 10 measurements).

3.2 Absorption and drying behavior

The water absorption of fresh Maastricht limestone specimens, before and after treatment, is reported in figure 9. The water absorption of the fresh stone decreases after treatment with ethyl silicate; a reduction of about 40% of the Water Absorption Coefficient (WAC) is measured.

Also for the re-aggregated specimens, a reduction of the water absorption rate is measured after treatment, though less pronounced than for the fresh stone specimens. In this case, it is difficult to quantify the effect of the ethyl silicate on the WAC, since the first part of the absorption curve of the treated specimen is not linear.

In the evaluation of the compatibility of a surface treatment, the effect of the product on the drying behaviour is of primary importance. A consolidant treatment should not considerably delay the drying [4].

The results of the drying measurements (figure 10) show that the ethyl silicate slightly delays the drying, both in sound and re-aggregated specimens: after 14 days the untreated specimens (both fresh and re-aggregated stone) have lost 99% of the absorbed water, whereas the same specimens, after consolidation, have lost 95% (fresh stone) and 92% (re-aggregated stone) of the absorbed water. This represents a slight delay in the drying which can be considered acceptable.

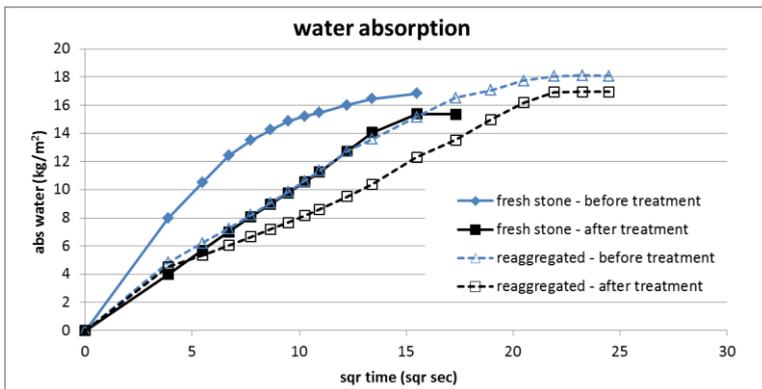


Figure 9: Water absorption of fresh and re-aggregated stone specimens, before and after treatment with ethyl silicate.

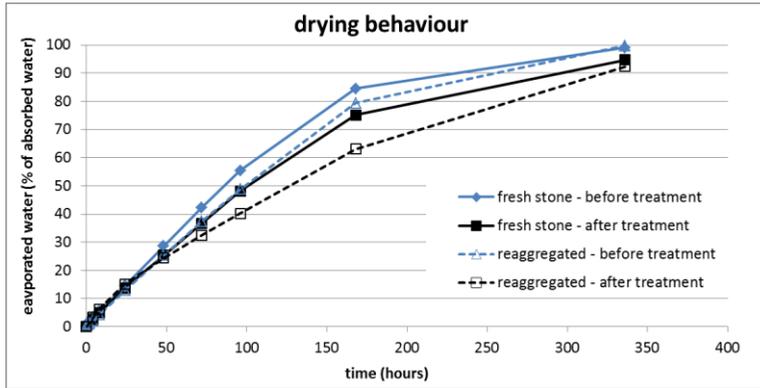


Figure 10: Drying behaviour of fresh and re-aggregated stone specimens, before and after treatment with ethyl silicate.

3.3 Salt crystallization test

The loss of material of re-aggregated specimens subjected to salt crystallization test during 4 complete cycles (about 12 weeks) is reported in figure 11.

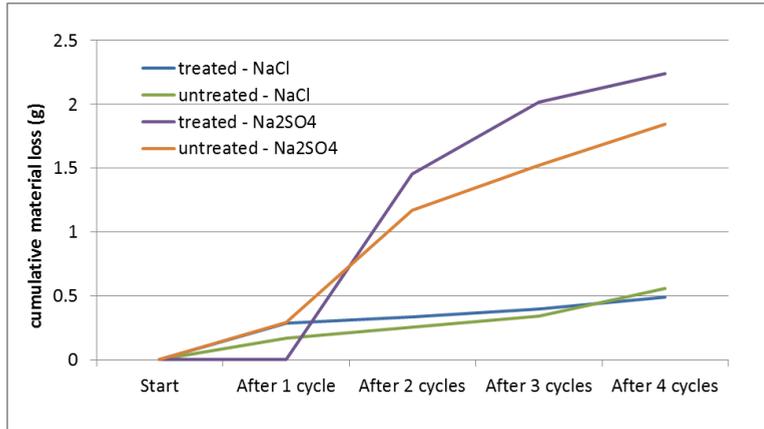


Figure 11: Cumulative material loss in specimens with re-aggregated layer during the salt crystallization test.

The specimens wetted with demineralized water (treated and untreated) did not suffer any damage. In the case of specimens contaminated with sodium chloride, very little damage was observed in untreated and treated specimens in the form of powdering of the surface. The specimens

showed a salt crust at the surface at the end of the drying period; the salts dissolve and migrate back into the specimen during the high RH periods.

The specimens contaminated with sodium sulfate showed a significant material loss. Damage appeared after the first (in untreated specimens) or second (in treated specimens) re-wetting. This is due to dissolution of thenardite followed by rapid re-precipitation of mirabilite at high supersaturation, with consequent generation of high crystallization pressures [15]. Most probably, the strengthening provided by the consolidant initially delayed the occurrence of the damage in treated specimens. However, after 4 re-wetting cycles, the loss of material in specimens treated with ethyl silicate was more relevant than in untreated specimens. Material loss occurred in the form of powdering of the re-aggregated layer in the case of the untreated specimen, whereas in the case of the treated specimen, a complete layer of about 2-3 mm thickness detached, due to the pressure developed by the crystallization of the salts accumulated under the outer layer. The thickness of the detached layer does not correspond to the full impregnation depth of the treatment (which is much deeper), but to the zone showing a very high strength in the DRSM profiles, due to an enrichment in ethyl silicate (figure 8). Most probably, the inhomogenous distribution of the treatment caused discontinuities in the moisture transport, which led to salt accumulation behind the zone rich in ethyl silicate and to development of locally high crystallization pressures and damage. In the untreated specimens, the more homogenous distribution of the salts beneath the surface, explains the observed limited damage in the form of powdering.

For comparison, the crystallization test was also carried out on fresh stone, treated with ethyl silicate and contaminated with sodium chloride and sodium sulfate. As for the re-aggregated specimens, no significant damage was observed in the case of sodium chloride. Specimens contaminated with sodium sulfate showed only 1/10 of the material loss observed in the specimens with re-aggregated layer, occurring in the form of powdering. No layering of the surface was observed, in spite of the clear enrichment in ethyl silicate in treated fresh stone noticed in the DRMS profiles (figure 7). It is not possible to foresee whether layering would occur in a later stage, after a larger number of cycles.

However, it is clear that significantly different results on the effects of a consolidant on the resistance of a material with respect to salt weathering can be obtained, depending on the state of conservation of the specimens (fresh or decayed) on which the consolidant is tested. This consideration underlines the importance of using (artificially) decayed specimens when testing the behaviour of consolidant products.

4 Discussion and conclusions

This research investigated the effect of an ethyl silicate product for consolidation of limestone on the resistance of Maastricht limestone to salt crystallization damage. With this aim the product was tested on fresh stone, as well as on specimens with a re-aggregated stone layer, constituting artificial analogues for decayed stone.

The results showed that this product applied on Maastricht limestone is able to reach a very deep penetration and to confer a significant strengthening to the substrate without significant altering the overall drying behavior of the material. However, a not homogenous distribution of the product and of its strengthening effect occurs in the impregnated zone. This has led, in the case of specimens with a re-aggregated layer, to salt accumulation behind the surface zone with accumulation of ethyl silicate, resulting in the detachment of this 2-3 mm thick layer.

The parallel execution of the salt crystallization test both on fresh stone and on re-aggregated specimens (reproducing the decayed substrate) has shown that the initial state of conservation of the substrate can significantly affect the results. Considered that in the conservation practice consolidant treatments are applied on decayed substrates, consolidants should be tested on (artificially) decayed substrates or on representative and reproducible replicas of these (as done in this research) in order to obtain reliable results with respect to their performance and compatibility.

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