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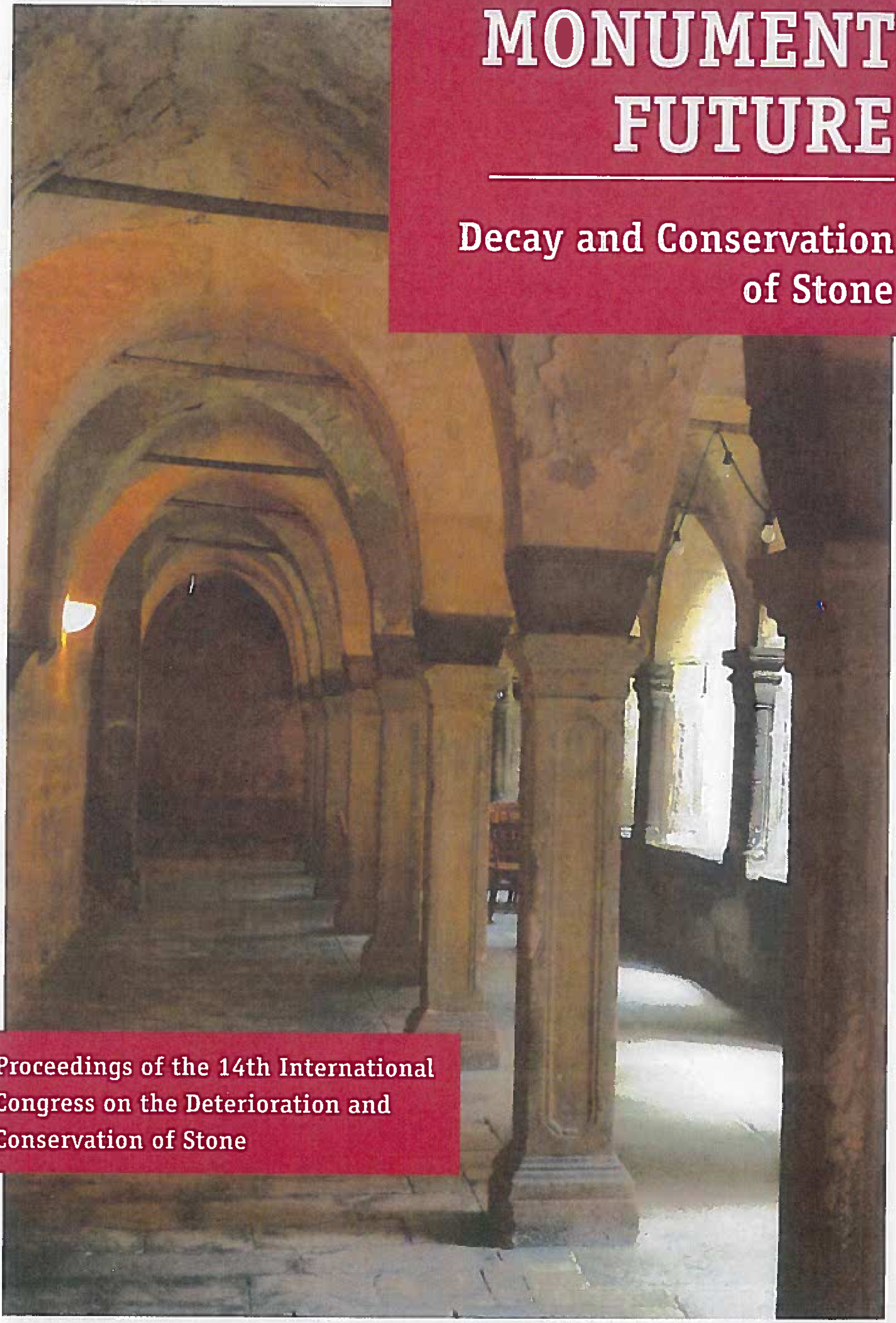
MONUMENT FUTURE

Decay and Conservation of Stone



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SILICATES FOR THE CONSOLIDATION OF STONE: NANO SILICA VS. ETHYL SILICATE

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Abstract

Stones used in monuments and historic buildings outdoors are usually affected by weathering which frequently leads to microstructural defects in the affected zones. Appropriate consolidants need to fulfil several requirements related to important issues of efficiency and compatibility.

In frame of the EU H2020 research project 646178 Nano-Cathedral, a series of potential stone consolidants based on inorganic nano-materials were tested against commercially available ethyl silicate systems. Since some of the most promising nano consolidants were found within the group of silicates with or without minor amounts of other types of functional nano particles, this paper focuses on silicate systems and attempts comparing the basic performances of nano silica sols vs. ethyl silicate (TEOS) products for a number of lithotypes. The consolidants were tested within an extensive laboratory program based on artificially aged stone specimens and loose aggregate samples, respectively. Parallel to tests of the physico-mechanical properties of treated vs. untreated stones, SEM on polished sections played a major role in evaluating the performance. The results are of interest in two ways: (1) they yield insight into the correlation between microstructural observations of consolidated pore systems and selected physico-mechanical test results (2) general advantages and shortcomings of nano suspensions compared to reactive TEOS were identified: lower rates of shrinkage and hence a better adhesion to the grains as well as higher bridging capacities are the benefits of the nano systems tested. For a number of decay patterns it proved therefor advisable to combine these characteristics through two-stage treatments.

Introduction

Silicates play a major role amongst currently available stone consolidants. Nature and properties of the various silicate products in their liquid state differ between reactive ethyl silicates (TEOS) and silica sols or nano-silica of varying particle size and concentration, dispersed in various liquids. The specific property of a silicate system in its liquid state governs primarily its penetration capacity into porous solids where silica gel forms through sol-gel processes. In the case of TEOS, this process takes place by hydrolysis and condensation, while silica sols turn to gels by evaporation of the respective liquid phase (Wheeler G. 2005, Zornoza-Indart A. et al. 2016). The binding and bridging capacity of such a gel inside a given pore system varies, amongst others in function of several factors linked to the original nature of the product, the way of sol-gel formation, and the concentration of the silicate. Aim of the study is to highlight the specific features of both types of gel within the pore systems of different lithotypes with regard to their respective states of weathering.

Materials and test methods

Development and testing of a consolidation system taylored for a specific stone with its characteristic decay features requires adequate test specimens to be included in extensive test protocols (Laurenzi Tabasso M. et al. 2006). For the statistical determination of physical and mechanical properties, the use of homogeneously, hence artificially aged stones of defined dimensions is often unavoidable. Artificial ageing creates microstructural defects without full destruction of the specimen, however, the micro-cracks induced by such procedures, especially in case of compact stones, are often not wide enough to allow for full impregnation by consolidants. Nevertheless such fissure systems are representative of defects frequently encountered in the outdoor weathering of compact stones, which is why such substrates proved useful in the laboratory program (Ban M. et al. 2016). However, for strongly weathered stone surfaces which show decay phenomena such as e.g. heavy disintegration, other test substrates are certainly required. Specimens which simulate such decay were based on the idea to mimic two different zones within a sample. In view of this, loose aggregates of the respective lithotype were placed on a slab of the same stone, with the aim to achieve consolidation of the disintegrated zone and a bonding to the compact stone. Since the use of different test specimens is often the best solution for establishing a suitable consolidation concept, as both the properties in terms of more compact and deteriorated material can be highlighted, in the present work both types of samples, laboratory aged (LA) and aggregate samples (A) were treated with commercial TEOS systems (KSE of different gel deposit rate by Remmers, Germany) as well as with modified TEOS (HFES70, based on ethyl ester of silicic acid with 70% active content and addition of 1% nano-TiO_2 dispersion in isopropanol by Chem Spec, Italy) and silica sol (ZG12, nano-SiO_2 suspension with particle size of ~70 nm in water-ethanol by Colorobbia, Italy). The latter ones were developed in the frame of the EU H2020 research project 646178 Nano-Cathedral (Coltelli M.B. et al. 2019). Furthermore, combined treatments of nano-sols and TEOS (ZG12 and KSE) were tested in view of more complex and severe decay phenomena. Even if silicate consolidants chemically tend to be incompatible with carbonatic stones, good results in practice are often reported (Wheeler G. 2005). Furthermore, other than TEOS there are at present no strengthening agents for highly porous limestones suitable for in-depth consolidation of up to several centimetres. Therefore, the lithotypes included in the test series covered a wide range of limestones, sandstones and marbles used on stone monuments in Europe, the results of which can only be mentioned here selectively. Polished sections of all treated specimen types (LA, A) were produced and examined by means of scanning electron microscope (SEM), whereby the spatial in-depth distribution, the adhesion to the substrate, possible bridging and shrinkage behavior of the respective consolidants were in the focus of interest. With respect to the physico-mechanical properties, a large number of test methods were applied (Ban M. et al. 2019), with particular emphasis on dynamic modulus of elasticity and fracture behavior compared to microscopic analyses.

Key test results for TEOS and silica sol

One of the prerequisites for successful consolidation is the penetration of the strengthener into the decayed material, although the final distribution of the solid consolidant is the determining factor for the result. In this context, the penetration behavior of all TEOS products can generally be classified as very good, though this depends strongly on the porosity of the treated stones and the type of test specimens used, i.e. LA or A. In the A-samples which stand for a decohesive layer above the sound stone, all TEOS products show an almost 'uncontrollable' penetration in a way that especially porous lithotypes tend to soak off the consolidant from the aggregate layer even hours after the application. With respect to the distribution of TEOS gel in the pore space a thoroughly homogeneous distribution over the full depth of 5 cm can be observed by SEM for LA-test specimens with purely microstructural defects. This also holds for the A-test specimens, but here the gel was not only detected within the aggregate layer but also frequently in the sound material beneath. This effect may result in an undesired 'over-strengthening' of the intact fabric. On the contrary, in the case of LA-specimens, the ZG12 gel can be found down to the full depth just in a few samples. Even though the penetration depth of the silica sol is in most cases less (3–4 cm) than that of TEOS, it shows the ability to penetrate into the finest pores as well as into cracks of 1 µm or smaller. In any case, the gel reveals a tendency to accumulate in areas of the treatment surfaces or even to form layers on the surfaces. On the other hand, no undesired penetration of ZG12 into the sound material of the A-specimens could be detected.

Even though penetration capacity and in-depth distribution of ZG12 tend to be rather poor, the gel exhibits excellent properties with regard to adhesion and bridging. These properties are probably due to the small particle sizes with high surface area and good chemical reactivity (Sierra-Fernandez A. et al. 2018). In all samples, irrespectively of the lithotypes tested, ZG12 with its excellent adhesion to the substrate proves a high capacity to form bridges between grains (Fig. 1).

Bridges with a width of up to 200 µm can be observed, they often show only fine shrinkage cracks. Bridges without cracks are generally 50 µm in size and below.

ZG12 does not cure in the form of plates either, but rather as an unstructured mass which adheres to the grain surfaces. These features are completely contrary to TEOS gels where the high degree of shrinkage is associated with poor adhesion (Fig. 2). Since the margins of their loose gel plates often follow the lines of the grain surfaces from which they are detached, or partly detachment of the uppermost grain layers can be observed by SEM (Fig. 2c), it is supposed that the gel detaches from the grain by shrinkage in the curing process. Even though TEOS products with increased contents of silica prove capable of forming gel plates in the range of 100–150 µm, 'real bridging' across pores of that size is never observed. In fact, 'crack-free' bridging can only be found up to a maximum size of 30 µm. With respect to the bonding properties it is further noticeable that the general assumption of TEOS being best applicable for silicate sandstones due to their chemical affinity, cannot be confirmed on the basis of microscopic observations. In the sandstone specimens investigated, the adhesion of the consolidant to the respective binder matrix of whatsoever mineral nature is always significantly better than to the coarse quartz grains which of-

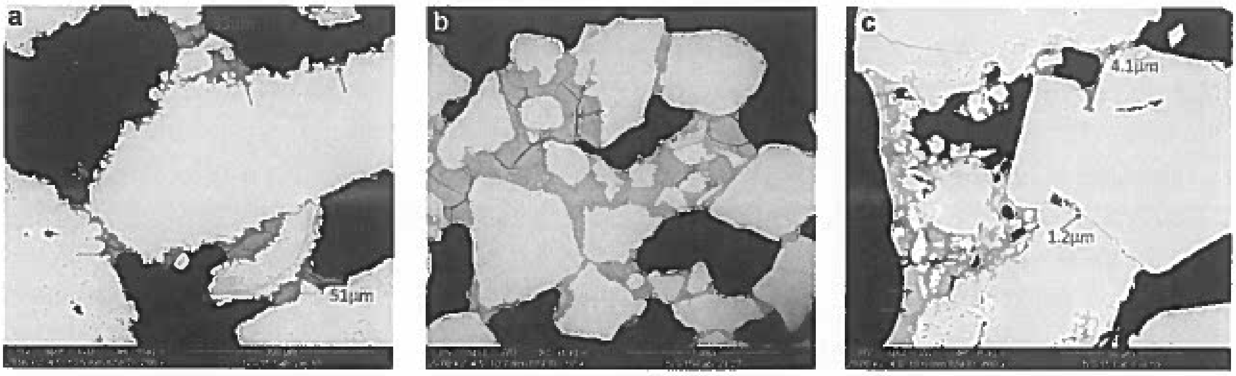

Figure 1: Treatments with ZG12, SEM-BSE images, the consolidant appears light grey. (a) Good adhesion and bridges up to 50 µm in treated LA-specimens of St. Margarethen detritic Limestone. (b) Treated A-specimens of Sierra Elguea Sandstone – very good adhesion to all grains with only minor shrinkage cracks. (c) Excellent adhesion to the fine-grained minerals of LA Obernkirchen Sandstone, however the surface is covered with a dense gel layer.

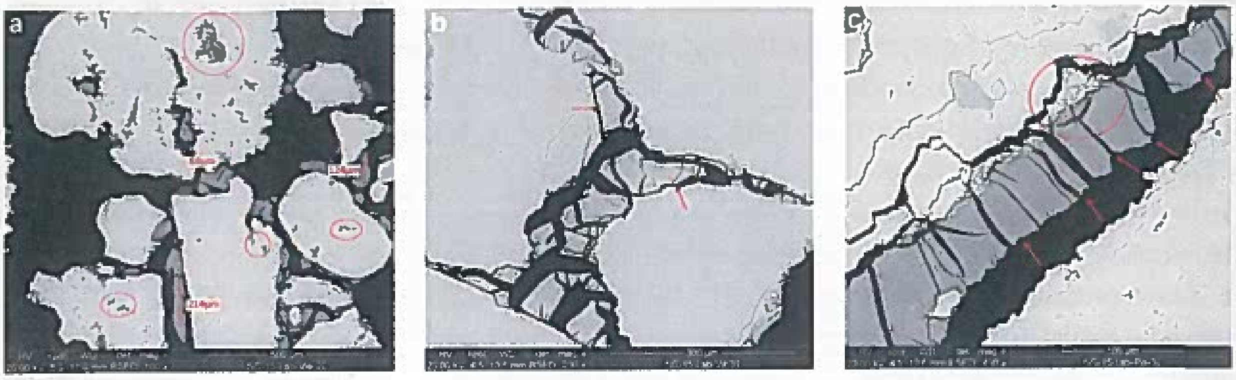

Figure 2: Treatments with TEOS, SEM-BSE images, the gel appears grey. (a) St. Margarethen detritic Limestone A-specimen, treated with KSE300 and KSE500E. Gel plates over 210 µm long, yet no bridging, depositions in intragranular pores. (b) Sierra Elguea Sandstone A-specimen, treated with HFES70. Very poor adhesion of large gel plates to the quartz grains, high shrinkage. (c) Monte Pisano Marble A-specimen, treated with HFES70. Shrinkage of gel has caused disruption of calcite on one side of the plate, and retraction on the other side.

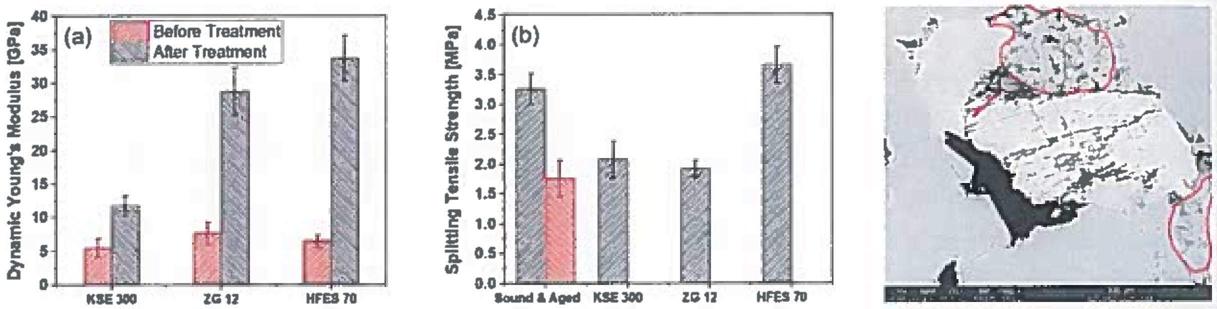

Figure 3: (a) Dynamic Young's modulus and (b) splitting tensile strength on the example of Schlaitdorf Sandstone, treated with different silicate consolidants. (c) SEM-BSE image of Schlaitdorf Sandstone with abundant kaolinite, treated with TEOS. Silica gel has preferably precipitated within the kaolinite matrix (marked red), while loose gel plates are visible in intergranular pores.

ten have lost their contact to the gel. Presumably, bonding is largely related to the morphology of the mineral surfaces. Thus, on uneven pore walls of detritic limestones, TEOS gels adhere significantly better, probably thanks to a kind of mechanical interlocking to the substrate.

The above addressed microscopic observations can be of use to interpret the results from mechanical tests. Fig. 3a/b illustrate readings from two different normative tests by the example of LA-specimens of a quartz arenite with abundant kaolinite, treated with two TEOS products (KSE300 and HFES70, respectively, and silica sol ZG12). By the dynamic Young's modulus (Fig. 3a), the consolidants proved efficient in all cases, that is, an increase in mechanical strength after each treatment was recorded, with the factor of efficiency clearly dependent on the silica content in each of the products. While these results might be due to the partial pore filling by the gel, the gel in itself may still exhibit low strength. This would then cause a mechanical failure visible through macroscopic mechanical tests such as the splitting tensile strength (Fig. 3b), the results of which are in discrepancy with the former one. In particular KSE300 and ZG12 treated specimens reveal lower splitting strength, obviously due to their lower silica content as compared to HFES70. Moreover, the texture of the substrate proves to be of importance when assessing the efficiency of a consolidant. In the present case of the quartz arenite, TEOS silica gel can preferably be detected in the kaolinite matrix by means of SEM (Fig. 3c). As the kaolinite is homogeneously distributed in the fabric, and preferentially consolidated, the mechanical strength gain could be mainly attributed to this consolidating phenomenon.

As a matter of fact, the active content in each of the test products obviously influences the results. In principle, the individual products can be optimally employed for different pore sizes or degrees of deterioration due to the different gel deposit rates. In particular, the newly developed product HFES70 can be of great importance for some decay patterns due to its extremely high active content.

Principle aspects of sequential applications of silica sol and TEOS

Since most weathering mechanisms lead to microstructural alterations with strongly differing petrophysical properties along profiles from the surface to the interior, it is understandable that just one product cannot always handle such complex tasks. Even when, with different brands of a product family (e.g. the KSE100, 300 and 500E TEOS systems by Remmers), complex consolidation issues can be mastered (Remmers 2019), there are yet no satisfying results in cases of particularly pronounced surface decay of a weathered stone.

This applies e.g. to severe granular disintegration, scaling or flaking. Due to the lack of sufficient adhesion of the silica gel to the grains, larger gaps cannot be bridged, and loose structures cannot be cohered (Dobrzynska-Musiela M. et al. 2018).

For laboratory tests, the use of A-samples is a suitable method of imitating such disintegrated zones which have to be consolidated and adhered to the sound stone underneath. Using these samples, different combinations were tested, which included among others a consecutive treatment of ZG12 and TEOS (KSE products) with an interval of one day. The evaluation was performed by SEM and sound speed propagation. For all stone varieties of the A-samples observed, the use of ZG12 and subsequent application of KSE (Fig. 4c) offers clear advantages in terms of adhesion to the substrate compared to the use of TEOS alone (Fig. 4b). On the other hand, the high shrinkage rate of TEOS products is positively influenced by an initial treatment with ZG12. Large shrinkage cracks which are common for pure TEOS treatments cannot be observed with the combined application. Furthermore, the combined treatment shows excellent results in terms of possible bridging properties. For the nano consolidant ZG12, which generally shows bridge formations of about 50 µm in width when the product is used alone, even larger bridges can be formed in combination with TEOS (Fig. 4a). Even if fine cracks are visible, in most cases the bridges are contiguous.

With respect to the sound speed propagation, the trend is the same for all consolidated aggregates, independent of the lithotypes used (Fig. 5).

It indicates that the combination of silica sol (ZG12) and TEOS (KSE300) has the most promising sound speed propagation when compared to the remaining combination of products or their solely use. The reason for this might be the combination of a good bridging capacity as seen in ZG12 and a

Figure 4: Sequential treatments with different silicate products of A-specimens from various lithotypes, SEM-BSE images, the gel appears grey. (a) Au detritic Limestone treated with ZG12 and KSE300. Bridging by gel with only minor shrinkage. (b) Balegem detritic Limestone treated with TEOS KSE300 and KSE500E. TEOS alone often prevents bonding of the gel to the grains, gel plates remain loosely in the pore space. (c) Balegem detritic Limestone treated with ZG12 and KSE300. Generally good bonding of the gel to the grains, only rarely prevented by shrinkage cracks within the consolidant.

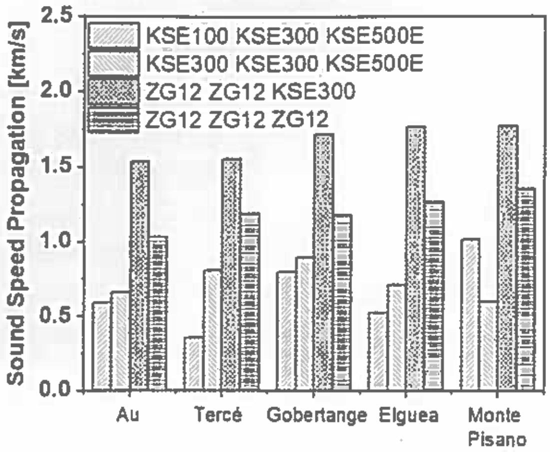

Figure 5: Sound speed propagation measured for A-specimens from various lithotypes treated sequentially with various silicate consolidants. Highest values are recorded for ZG12 sol treatments followed by TEOS KSE300.

good in-depth distribution usually observed within KSE300.

Summary

SEM investigations on polished sections of stone specimens treated with silica sol and TEOS showed that the consolidating silica gels precipitated in the pore space of various test specimens differ in terms of their topographic distribution, the rate of shrinkage and the adhesion to the grains of the substrates. While TEOS generally penetrates very well and the resulting gel is evenly distributed in the pore system, this is far less the case for the tested silica sol. On the other hand, the gel formed from sol product offers particularly good properties in terms of adhesion and low shrinkage as well as potential bridging capacities between the grains of the substrate. Thus, the combined use of both types of consolidant shows promising results and should be envisaged in the practice in order to remedy severe decay patterns. However, it must be clear that the results refer to the examined products only; any other silicate product would require tests on its own. To this end, the two types of test specimen used in the present study, i.e. thermally aged stone bodies and loose aggregate samples, have proved useful to cover a range of microstructural defects frequently encountered in outdoor weathering of stone. Further research including microscopy is needed to better understand the significance of mechanical bulk tests.

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