Article

Consolidating Efficiency of Nanolime Product CaLoSiL on Porous Limestone

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Abstract: The effects of the double and the multiple application (2 to 6) of Calosil® (IBZ-Salzchemie GmbH, Halsbruecke, Germany) E25, IP 25 and E50 products were studied on Maastricht limestone, which is characterized by high porosity and large pores. Both destructive and non-destructive laboratory tests we performed in order to assess the consolidating efficiency of the nanolimes—the bending and compressive strengths, ultrasound velocity measurement, porosity determination and SEM examination. Except for the compressive strength, the other characteristics were investigated in the depth profile of stone specimens to find the distribution of the treatment product within the substrate. The performed tests showed good penetration of CaLoSiL nanolime products into the studied limestone. The bending strengths of limestone samples after double treatment using nanolime E 25, IP25 and E 50 were found to be increased by 50%, 44% and 89%, respectively, whereas the compressive strength increased by 50%, 23% and 73%. The porosity of the stone was reduced by the treatment, but only slightly, to an acceptable extent. The higher sum of performed nanolime applications resulted in a higher strengthening effect but at the same time at the uneven distribution of the product in the stone specimen, which was followed by an increase in the strength and decrease of open porosity in the surface part. SEM examination showed a modification of the stone microstructure by the added binder.

Keywords: nanolime; calcium hydroxide; consolidation; strengthening; CaLoSiL; Maastricht limestone

1. Introduction

The recent increased interest in nanotechnologies has influenced conservation science and has seen nanoparticles of calcium hydroxide dispersed in alcohols as a new form of treatment product based on $Ca(OH)_2$. Suspensions containing lime particles in submicrometric dimensions were developed as an alternative to lime water, which has traditionally been used to consolidate mortars and calcareous stones [1,2]. Lime water treatment has some limitations, which include a particularly enormous number of applications due to $Ca(OH)_2$ low water solubility and reduced penetration depth [3,4]. Slížková et al. [5] investigated the efficiency of consolidation by various consolidants (lime water, nanolime, alkoxysilane-based agents) on lime mortar specimens with the conclusion that a significant consolidating effect was achieved by 78 applications of lime water whereas the same $Ca(OH)_2$ amount was impregnated in the mortar by 9 applications of nanolime suspension product (CaLoSiL IP 15) with a better strengthening result. The benefit of the nanolime treatment compared to that of lime water was that the same lime portion was introduced into the consolidated material without lots of water, was faster, and the treated object was not exposed to long-term moistening. Because of their chemical compatibility with calcitic substrates, nanolimes have been tested for strengthening carbonate stones, lime mortars and wall paintings [5–10].

Nanolime penetration depth monitored by roentgenography reached 20 mm [11], which is comparable to alkoxysilanes, but unlike them, nanolime appears to be chemically

compatibility with calcareous substrates. The efficiency of the consolidation is significantly affected by the nano-sized structure of the applied crystalline phases. The particle size influences their reactivity and penetration through porous matrices. Thus, it appears evident that the processes involved in the preparation of nanoparticles and their dispersion in carrier media all play fundamental roles in determining the final effectiveness and applicability of these conservation tools [12]. CaLoSiL® (introduced in October 2006) is the first commercially available stone treatment product based on calcium hydroxide sol [13,14]. The efficiency assessment and other research on this product in building materials treatment consolidation were carried out within the European project STONECORE [15]. Another commercial product, Nanorestore® (CSGI Consortium, Florence, Italy), was developed at the University of Florence (CSGI Consortium) and has also been studied by conservation scientists [16]. The nanolime transport mechanism within Maastricht limestone and the role of the solvent used during the consolidating process have been studied in the last decade. In order to achieve better penetration of the nanoparticles into the depth of the stone, lower boiling point alcohol solvents (such as ethanol or isopropanol) were used. These solvents have a high kinetic stability and create stable dispersions with the nanolime [17–19].

The effectiveness, harmfulness and durability of consolidation depend not only on the stone and products' characteristics but also on procedures adopted for their application. Application technique, number of applications, and the time interval between applications and ambient conditions before and after treatment can significantly affect the consolidating effect [20]. The manufacturers of consolidating agents usually provide instructions on how to apply the product, but the information is not always detailed enough. The study presented here is focused on researching the behavior of the Calosil® product that is available in the market with different $Ca(OH)_2$ concentration levels and with different types of alcohol as the dispersion medium. The potential user can read on the manufacturer's website [21] that for consolidation of objects with low porosity, the low concentrated products (Calosil® E5 or E15) are suitable, whereas for high porous objects, the more concentrated Calosil® E25 or E50 can be used. The pores' size of the material to be treated is not considered. Multiple applications of the consolidant are recommended if a higher strengthening effect is required and it is emphasized that it is always better to use a product with a lower concentration several times than a product with a higher concentration only once. We decided to validate this approach in an experimental laboratory study, where we chose a limestone with high porosity and large pore sizes to ensure good conditions for the penetration of even the most concentrated Calosil® product. Effects of the double and the multiple application (2 to 6) of Calosil® E25 respective E50 products were studied using the following destructive and the non-destructive laboratory tests: bending and compressive strengths, ultrasound velocity measurement and porosity determination. Except for the compressive strength, the other characteristics were investigated in the depth profile of stone specimens in order to find the distribution of the consolidating product in the treated stone sample. The testing was aimed especially at a quantitative assessment of the strengthening effect.

2. Materials

2.1. Treated Stone

The laboratory experiment was carried out on Maastricht limestone, a material with low mechanical characteristics, high open porosity and large pore sizes. These stone characteristics seemed to be suitable for such a consolidation study focused on stone strength enhancement. Despite its low mechanical strength, Maastricht limestone appears to have remarkable durability, given by frost resistance and recrystallisation of carbonates [22]. Upper Cretaceous Maastricht limestone ("mergel") outcrops in Dutch and Belgian Limburg provinces. Formation represents one of the few native Dutch natural stones used for building and construction. The Maastricht limestone is very homogeneous, and layering is rarely observed. The only location where the Maastricht limestone can be quarried today is in Sibbe, Holland. Under the optical microscope, the Sibbe variety shows good sorting

with a grain dimension of about 100 μm [22]. The subangular grains of sparitic calcite or micritic calcite are glued together by a calcitic binder. The porosity is high (about 50%) and mainly constituted by macroporosity (most pores have a diameter of 48 μm). The presence of large pores correlates with a high water absorption coefficient (20.2 $kg/m^2min^{1/2}$) of this stone [23].

2.2. Treatment Agents

Three variants of the commercial product CaLoSiL were used in the present study. The products contain $Ca(OH)_2$ particles dispersed in different alcohols (ethanol and isopropyl alcohol types were investigated). Before the experiment, the morphology of $Ca(OH)_2$ particles of nanolimes was studied by scanning electron microscopy. These observations confirm that the mean size of CaLoSil particles ranges from 50 to 250 nm and they have a regular hexagonal shape (Figure 1).
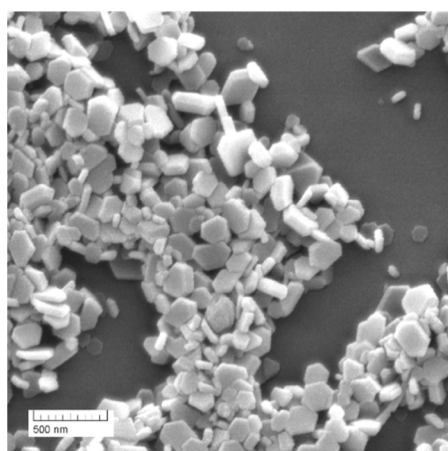

Figure 1. SEM micrograph of CaLoSil E 25 particles.

2.3. Application Procedure

Stone specimens were conditioned in a laboratory before the experiment. The treatment was performed on 5 × 5 × 3 cm prismatic specimens, and only one face of the specimen was treated with a particular volume of the product (30 mL). The product was applied by syringe, pouring the stone surface until the total volume of 30 mL of the product had been soaked. The volume (30 mL) was chosen as the amount of the product needed for the wetting of the 75 cm^3 (5 × 5 × 3 cm) stone specimen. The selected volume (30 mL) does not refer to the volume needed for full saturation of the stone but for its impregnation by capillary absorption when the front of the product (visible by the darkening of the impregnated stone material) reaches the bottom of the stone specimen. The time needed for the first and the successive applications (2–6) was measured.

Specimens for the bending test, ultrasonic velocity and porosity investigated in-depth profile were treated on the 5 × 3 cm face. Since the multiple application of the products was studied, two specimens were impregnated twice, another two specimens four times and the last two specimens six times. The break between every single impregnation represented four days. This time was sufficient for the drying out of impregnated stone under laboratory conditions, which had been found on the basis of an individual preliminary test. Stone specimens were not covered by any impermeable coating, which should control the evaporation of alcohol from the impregnated material, and so the drying process of the stone went through all specimen faces and was relatively fast thanks to the alcohol medium of the nanolime and also to a high and large stone porosity. Stone specimens were able to absorb 30 mL of the nanolime product even in the case of the sixth application, but the time needed for the repeated impregnation increased for some types of the CaLoSiL product.

Specimens for the compressive test had the same parameters (5 × 5 × 3 cm). These specimens were impregnated in the same manner as the previous specimens with one difference: the product was applied through the 5 × 5 cm face to a depth of 3 cm.

The maturing of impregnated stone specimens occurred in dry conditions (laboratory environment, 20–25 °C, 30–40% RH) without any special care. The testing of impregnated specimens started one month after the consolidation treatment.

Results from the performed tests are expressed as an average value gained from individual measurements of two specimens treated with the same procedure.

3. Methods

Research of the consolidating efficiency on rock materials typically involves testing of the change of their physical characteristics. The authors applied non-destructive as well as destructive approach for investigation of physical changes along the depth profile of the tested material after surface consolidation treatment [24]. Cutting a block of rock into thin plates is a solution that brings a number of advantages, as it allows for testing a number of physical properties on identical samples. In the presented case, only the bending strength and porosity values were acquired on thin plates; however, this methodology enables the testing of thermal and hygric expansion or vapor permeability, which are other important physical characteristics influenced by consolidation agents [25].

The ultrasonic velocity was measured with a portable instrument USG 20 (Krompholz Geotron Elektronik, FRG, Pirna, Germany) with a 250 kHz transmitter (USG-T) and receiver (USE-T). The measurement was taken in a direct transmission/reception mode across opposite parallel sides of the specimen. In the first step, the untreated stone specimens were measured in all three spatial directions (one measurement for the one axis) so that the difference between the X, Y and Z axes was found for each specimen and a unified geometric orientation for all specimens could be set before the treatment. Only one geometric plane was selected for a more detailed study. Then, the depth profile of ultrasound velocities was measured with a step of 7 mm in the direction from the treated top surface to the bottom (Figure 2). The measurement points were marked on the stone specimens, and the comparative test after the specimen treatment could be taken using the same points and tracks. The diameter of the flat contact area on the transducer was 2 mm.
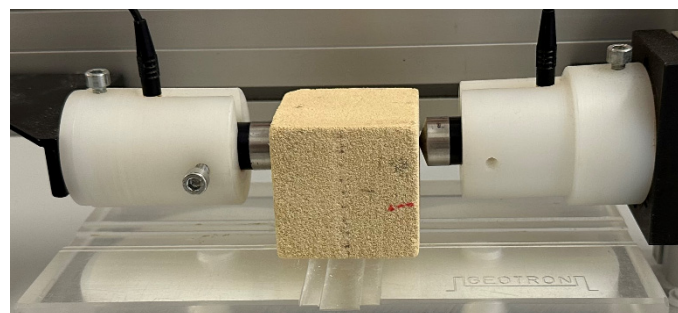

Figure 2. Ultrasonic velocity measurement.

The bending strength values in the depth profiles of not treated and treated specimens were tested on thin plates. The 50 mm depth was cut into slices, so eight thin rectangular plates at a depth of 3.7 mm ± 0.3 mm with the top side parallel to the surface were created. Slides were marked 1 to 8, and their specific positions relating to the original surface were registered. The bending strength and the Young's modulus of elasticity were then tested on these small-size partial specimens, which resulted in the knowledge of strength values in relation to the location of a stone layer in the original stone specimen. This way of testing enabled determining the strength values distribution along a depth profile perpendicular to the surface. The specimens were tested in three-point bending in a special rig after long-term conditioning in the laboratory (20–25 °C /RH 30–40%) using load cell Lucas

100 kN for the load measurement and LVDT 1 mm sensor for the deflection measurement, at the cross head speed of 0.15 mm/min.

The open porosity and pore size distribution in the studied materials were determined by Mercury intrusion porosity using a Quantachrome porosimeter (Quantachrome Instruments, Boynton Beach, FL, USA), model Poremaster PM-60-13, with a pressure range of 0.005–413 MPa. The mercury parameters were set to values of 480 erg/cm^2 for the surface tension of mercury and 140 degrees for the contact angle. The samples were dried out before the test, and a penetrometer of 1 cm^3 was used for the measurement. After performing the bending test, the broken stone slices were used for porosity characterization.

The hydric behaviour through the stone was studied on specimens $50 \times 50 \times 30$ mm^3 (treated surface 50×50 mm^2). The determination of the porosity accessible to water was carried out following RILEM recommendations [26].

The compressive strength was tested on identical specimens such as hydric characteristics using load gauge Lucas 50 kN, sensor Megatron 25 mm, and load speed 0.45 mm/min.

In order to analyze the morphology, particles' dimensions and crystallinity, nanolime, both nanolime products alone and applied on Maastricht limestone, were investigated by a MIRA II LMU scanning electron microscope (Tescan Corp., Brno, Czech Republic). Samples of nanolime suspensions were prepared by placing a drop of consolidant on glass and drying the nanolime drop under a vacuum. Samples of nanoparticle-impregnated Maastricht limestone were fractured and the fracture surface was observed in SEM. All samples were carbon-coated prior to microscopic investigation. Samples were investigated in BSE mode at 7 kV accelerating voltage.

4. Results and Discussion

4.1. Penetration Time

The time needed for the first and for each successive application (2–6) indicates a possible change of transport characteristics of the CaLoSiL within the stone in the case of repeated applications. The best results were obtained for the CaLoSiL E 25, which needed roughly the same time (around 300 s) to penetrate the specimen from top to bottom for the first and the following applications. Simple measurement showed that even in the case of the sixth application, the penetration coefficient of this product did not change significantly. Figure 3 illustrates the different behaviours of tested products.
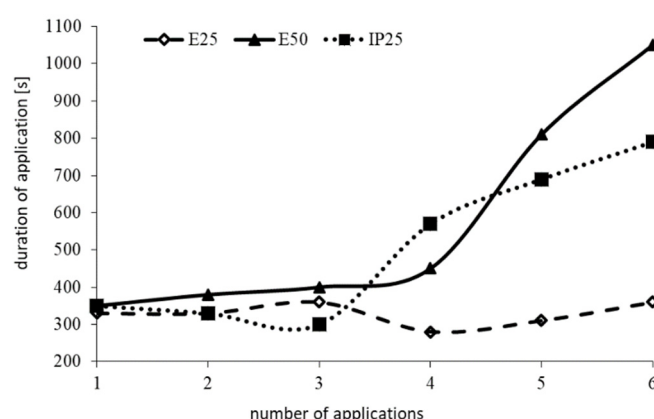

Figure 3. The time needed for wetting a stone specimen with 30 mL of CaLoSiL to the number of successive applications.

For the CaLoSiL IP 25 and E 50, the time needed for specimen impregnation increased after the first three applications as the product penetration ability got worse, especially in the case of the highly concentrated CaLoSiL E 50. The accumulation of these products in some parts of the stone specimen is probably the reason for the rise of the penetration time in the cases of the fourth to the sixth application.

4.2. Ultrasonic Velocity (USV)

The determination of the USV profiles is a method often used [27,28] to estimate the distribution of the product's effective compound (calcium carbonate in this case) developed within the stone specimen after the treatment and this non-destructive method was also applied also in our study. Since consolidants are supposed to change the stone porosity and mechanical properties, the ultrasonic velocity is usually considered as a good diagnostic tool to trace these changes [20]. The US velocity in the untreated specimens was 1.7–1.8 km/s, and the profile was relatively homogenous. Most of the treated specimens showed an increased velocity in the surface area (top and bottom), probably as a result of the accumulation of the consolidation product during the evaporation period (Figure 4).
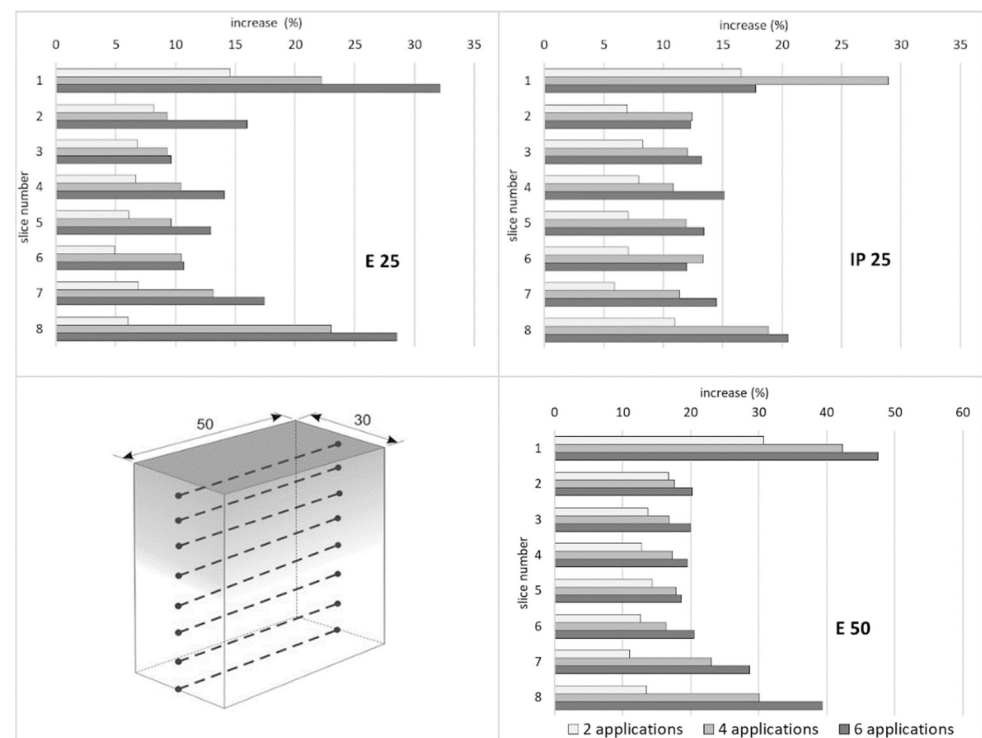
Figure 4. Ultrasound velocity increase in the depth profile for the Maastricht limestone after treatment with CaLoSiL IP 25, CaLoSiL E25 and CaLoSiL E 50 with the layout of the US velocity measurements (left down) from the top (point 1) to bottom (point 8).

The rise of USV due to the treatment represents about 5% of the original value in a central part of a specimen for the lower concentration and about 13% for the higher concentration after two applications. In the surface area, the increase of velocity was 2–3 times higher compared to the central part of the stone. The consolidating effect (US velocity) increased more after successive applications (4–6) but more intensively in the area near the surface. It seems from the USV measurements that multiple applications of the CaLoSiL products led to the accumulation of the product within the surface region, and this trend is more significant in the case of the higher concentrated studied type—CaLoSiL E 50. The optimal procedure for consolidation of the investigated stone seems to be two applications of the lower concentrated types—CaLoSiL E 25 or IP 25. Different behaviour of the products E 25 and IP 25 has not been found in the case of the USV tests; the differences between the velocity profiles are pretty low for both products with a different alcohol medium.

4.3. Bending and Compression Strength

The US velocity corresponds with the stone modulus of elasticity and characterizes its change resulting from the consolidating treatment very sensitively. Bending strength

profiles (Figure 5) brought similar results, but in detail, these data have a higher scatter, which is probably influenced by local defects. Considering the distribution of the strength in the profile, better results were found on the stone consolidated by two applications only. The higher number of applications went to an uneven distribution of the product in the stone, which was followed by an increase of the strength in the surface part.
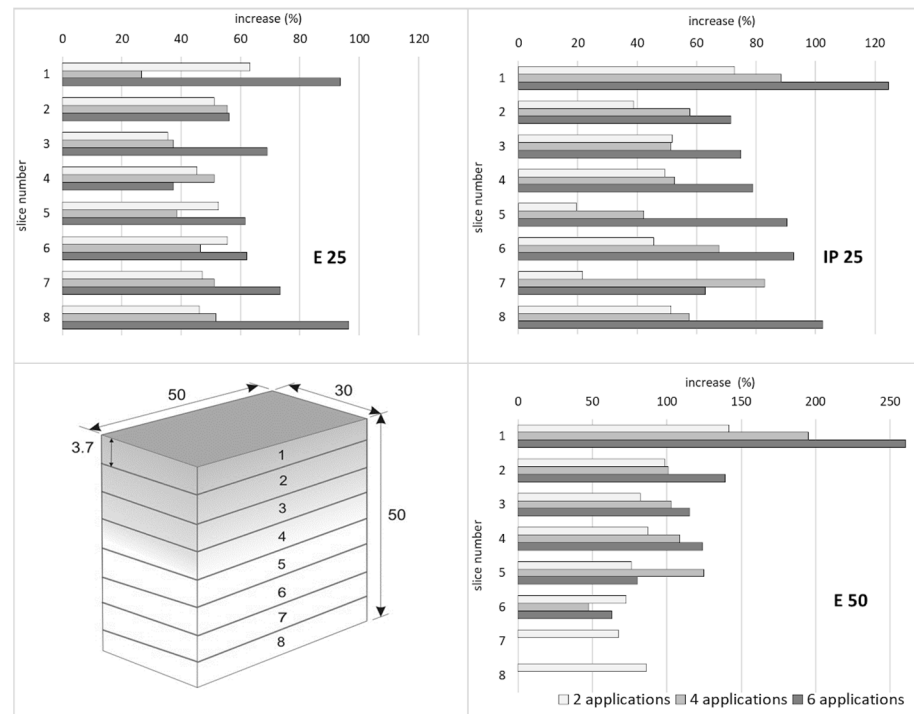

Figure 5. Bending strength increase in the depth profile for the Maastricht limestone after treatment with CaLoSiL IP 25, CaLoSiL E25 and CaLoSiL E 50 with the layout of a specimen cutting to slices for detailed bending strength tests (left down) from the top (slice 1) to bottom (slice 8).

The strength increase of overall stone specimens is illustrated in Figure 6 for both the bending and the compressive strengths. The distribution of the strength in the stone specimen profile is not considered in these graph; the average values of the specimen strength are shown (for the bending, the average is calculated from individual slices strength of two specimens, and the compressive strengths were determined by testing two specimens $5 \times 5 \times 3$ cm).

The increase of the average bending strength value of a specimen represented 77% after six applications for E 25, 108% for IP 25 and 130% for E 50. The rise of compressive strength was 93% for E25, 47% for IP 25 and 126% for E 50 after six applications. After two applications (which seems to be a suitable treatment amount relating to the even distribution of the product in the stone), the bending strength increase represented 50% (E 25), 44% (IP 25) and 89% (E 50) and the compressive strength increase was 50% (E 25), 23% (IP 25) and 73% (E 50). The presented test results support the conclusions that two applications of the CaLoSiL products seem to be the optimal procedure for treating porous limestone. When a stronger strengthening is needed, the higher concentrated product E 50 applied with care may be useful.

Even though the destructive character of mechanical strength tests does not allow the performance of these tests before and after the treatment on identical specimens, a quite good homogeneity of stone along the selected axis enabled the evaluation of the strengthening effect by means of comparing the strength values obtained on different not treated specimens and different treated specimens of the same type of stone.
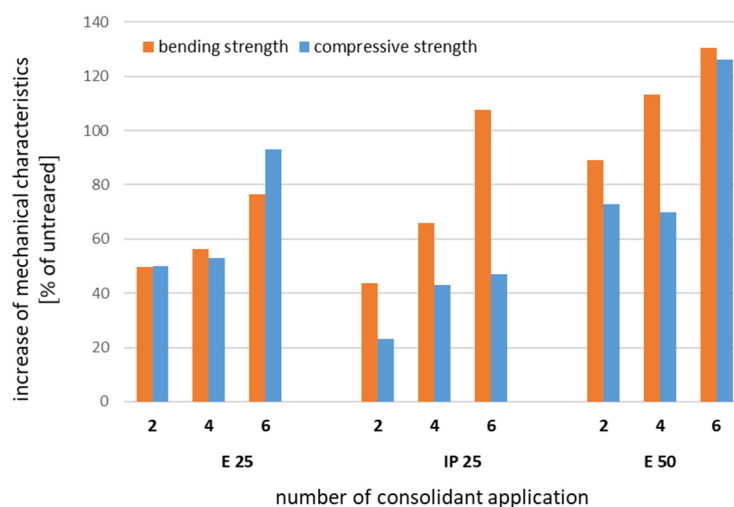
Figure 6. Increase of bending strengths (orange color) and compressive strengths (blue color) of the Maastricht limestone caused by consolidation with CaLoSiL products applied multiple times.

4.4. MIP and Water-Accesible Porosity

The porosity investigations correspond with previous results. The values of the open porosity obtained on a specimen $5 \times 5 \times 3$ cm were quite promising; the porosity decreased due to the treatment but not dramatically—from 50.3% to 47.4% (for stone treated with E 25 or IP 25 six times). This result is in accordance with the requirement of a small or moderate decrease of porosity caused by consolidation treatment [29]. The MIP method used for testing porosity in the depth profile showed its uneven distribution coming from a more significant influence on pores near the surface (Figure 7), even after two applications.
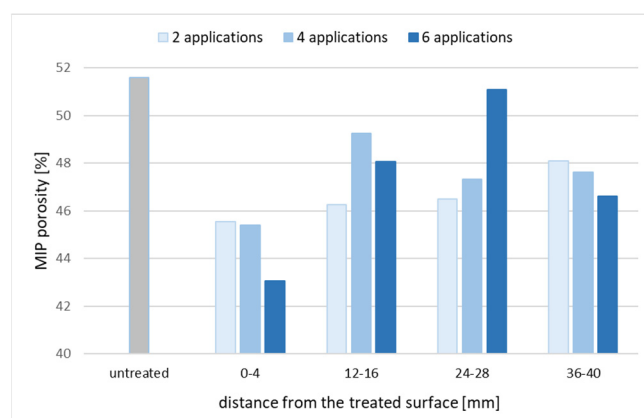

Figure 7. Distribution of open porosity values (MIP) within the specimen depth profile and treatment through CaLoSiL E 25—2, 4 and 6 applications.

4.5. SEM Observation

SEM images provide qualitative evidence of the microstructure of stone samples before and after the treatment. The representative images of the untreated stone and the stone twice treated with CaLoSil E 25 were selected and are presented in Figure 8. For natural stone, the images showed calcitic grains with mostly subangular shape and a size around 100 μm. The scalenohedral crystalline structure of grains and various shapes of pores with the size up to 50 μm are visible at higher magnification (Figure 8b). For the images of treated stone, results indicate a decrease of open pores quantity due to stone impregnation. The grains are covered with a thin opaque layer of the added binder and the intergranular space is more filled with the new binder. Only part of the original pore space remained open after the treatment. Figure 8d shows the detail with a higher degree of pore

filling, where the grains are almost completely connected by a new binder. SEM images of samples with more intense impregnation (higher $Ca(OH)_2$ concentration, more doses) show, especially in the surface area of the sample, a thick layer of new binder on the grains and a higher degree of pore filling.
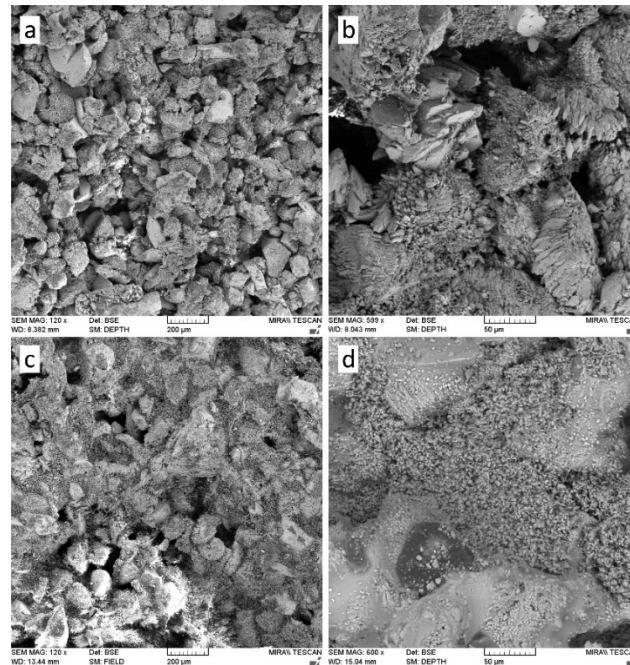

Figure 8. Microstructure of Maastricht limestone before the treatment (**a**,**b**) and after the double treatment with CaLoSiL E 25 (**c**,**d**). SEM images in BSE mode show modification of stone microstructure by filling the pores with a new binder.

4.6. Colour Change

Concerning the stone colour (Figure 9), the local white hazes appeared on the surface of some specimens (IP 25 and E 50 after six applications of the products). Colour change to this level cannot be accepted in common cases. White staining was not found for specimens treated with the CaLoSiL E 25.

Figure 9. White haze formation on Maastricht limestone after 6 applications of CaLoSil IP25.

The effect is connected to the evaporation of the solvent, which results in partial back-migration of the nanolime particles towards the exposed surface. Borsoi et al. [18] observed a dense nanolime deposition at 0.5 mm from the exposed surface of limestone treated with nanolime. This phenomenon is affected by the evaporation rate, i.e., environmental

conditions and kind of solvent, or a solvent's boiling point. To circumvent this problem, a simple procedure enabling better control of the consolidation depth profile was suggested by the authors in a previous paper [11].

5. Conclusions

The performed tests showed good penetration of CaLoSiL nanolime products into the studied limestone with large pores (diameter of 48 μm). Evaluation of the consolidation effect using USV, bending strength, porosity and SEM examination leads to the conclusion that treatment with a lower concentrated nanolime product (CaLoSiL E 25 or IP 25) causes a better distribution of the new binder in the stone. The bending strengths of limestone samples after double treatment using nanolime E 25, IP25 and E 50 were found to be increased by 50, 44 and 89%, respectively.

The porosity of the stone was reduced by the treatment, but only slightly, to an acceptable extent. Application of the products with a different alcohol medium (CaLoSiL E 25 and IP 25) generates relatively low observed differences measured by the ultrasonic velocity and the bending strength in the depth profiles. SEM examination showed modification of stone microstructures by the added binder. Stone grains were covered with a thin opaque layer and the intergranular space was more filled.

The higher sum of performed nanolime applications resulted in a higher strengthening effect but at the same time at the uneven distribution of the product in the stone specimen, which was followed by an increase in the strength and decrease of open porosity in the surface part. In the case of the most intensive treatment (6× with IP 25 or E 50), an unacceptable colour change occurred in the form of white spots appearing on the treated stone surface.

The challenge for further research is the development of calcium hydroxide or calcium carbonate nanosuspensions with even smaller particle sizes (from units to tens of nanometers), which would penetrate even denser types of limestone and calcium carbonate-based substrates.

Author Contributions: Conceptualization, Z.S.; methodology, Z.S. and M.D.; formal analysis, Z.S., D.F. and M.D.; investigation, Z.S., D.F. and M.D.; resources, Z.S.; data curation, Z.S., D.F. and M.D.; writing—original draft preparation, Z.S.; writing—review and editing, Z.S. and D.F.; visualization, D.F.; supervision, Z.S. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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