

## CONSOLIDATION OF POROUS LIMESTONE WITH NANOLIME LABORATORY STUDY

Zuzana Slížková<sup>1</sup> and Dita Frankeová<sup>1</sup>

<sup>1</sup> *Institute of Theoretical and Applied Mechanics, Academy of Sciences of the CR*  
*[slizkova@itam.cas.cz](mailto:slizkova@itam.cas.cz) [frankeova@itam.cas.cz](mailto:frankeova@itam.cas.cz)*

### Abstract

Effects of a lower and a higher concentrated nanolime product CaLoSiL after its multiple applications on porous limestone have been studied and presented in the paper. The assessment of the consolidating efficiency of the products was based on performance of both the destructive and the non-destructive laboratory tests: bending and compressive strengths, ultrasound velocity measurements and porosity determination of stone specimens. Concluding the test results performed for the depth profiles of specimens, two applications of the CaLoSiL E 25 or IP 25 products seem to be an optimal procedure for treatment of the studied porous limestone. Further applications of the product especially in the case of the higher concentrated CaLoSiL E 50 resulted in an uneven distribution of the measured characteristics (strength and porosity) due to an accumulation of the consolidating product near the surface. The appropriate amount of the product (both the concentration of the effective compound and the sum of the product applications) should be chosen in relation to the stone porosity and the treatment condition in order to achieve a regular distribution of the product in the substrate.

**Keywords:** nano-lime, calcium hydroxide, consolidation, strengthening, CaLoSiL, stone

### 1. Introduction

The recent outburst of nanotechnologies has influenced the conservation science and has brought nanoparticles of calcium hydroxide dispersed in alcohols as a new form of treatment product based on  $\text{Ca}(\text{OH})_2$ . Nanolime products are an attractive choice mainly for the consolidation of substrates containing calcite considering the intended chemical compatibility between the treated substrate and the treatment product. CaLoSiL® (introduced in October 2006) has been the first commercially available stone treatment product based on calcium hydroxide sol (Ziegenbalg 2008; Drdäcký et al. 2009). The efficiency assessment and other research of this product in the field of building materials treatment consolidation were carried out within the European project STONECORE (2009-2011). Another commercial product Nanorestore® was developed at the University of Florence (CSGI Consortium) and has been also studied by conservation scientists (e.g. López-Arce et al. 2010). Consolidation action depends on the products' characteristics but also on procedures adopted for their application (Ferreira Pinto et al. 2008). This paper presents the influence of the repeated application (1 to 6) of CaLoSiL products of the lower and the higher concentration of  $\text{Ca}(\text{OH})_2$  on the stone with high and large porosity.

## 2. Research aim

The treatment product CaLoSiL® is available in various concentration of  $\text{Ca}(\text{OH})_2$  from 15 to 50 g/l in different alcohols. However this product brings a much more effective alternative in relation to lime water (Drdácký and Slížková 2008), the concentration of the effective substance in the product is low when compared to the products based on silicic acid ester (100-500g/l). Multiple applications of the CaLoSiL product can be considered when a higher consolidation effect is required (Drdácký and Slížková 2011). This can be achieved either by multiple application of a low concentrated CaLoSiL or using a high concentrated product. The presented research studied differences in the both approaches when applied on a porous limestone. The assessment of the consolidating efficiency of the products was based on performance of both the destructive and the non-destructive laboratory tests: bending and compressive strengths, ultrasound velocity measurement and porosity determination. Except of the compressive strength the other characteristics were investigated in the depth profile of stone specimens in order to find the distribution of the treatment product within the substrate. The testing aimed at a quantitative evaluation of the product strengthening effect and at a recommendation of an optimal treatment procedure for the selected type of stone and treatment condition (dry condition T 20-25°C, RH 30-40 %).

## 3. Materials and Methods

### 3.1. Treatment products

Three variants of the commercial product CaLoSiL were used in the present study. The products contain  $\text{Ca}(\text{OH})_2$  particles dispersed in different alcohols (ethanol and isopropyl alcohol types were investigated). The particles size ranges from 50 to 150 nm. The producer of the agent is IBZ-Salzchemie GmbH & Co. KG, Germany. In the study an ethanol based type with two different concentrations of dispersed lime particles (25g/L, 50g/L respectively) and an isopropyl alcohol based type with concentration 25 g/L were examined. Trade names of the selected types are CaLoSiL E 25, CaLoSiL E 50 and CaLoSiL IP 25. The behaviour of differently concentrated CaLoSiL and the influence of a different alcohol medium were studied at consolidation of a highly porous limestone aiming improvement of material (calcite crystals) cohesion.

### 3.2. Stone

The laboratory experiment was carried out on the Maastricht limestone (Table 1), which is a material with low mechanical characteristics, a high open porosity and large pore sizes. These stone characteristics seemed to be suitable for such a consolidation study focused on the stone strength enhancement. Upper Cretaceous Maastricht limestone ("mergel") outcrops in the provinces of Dutch and Belgian Limburg. 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 (Rescic et al. 2010) the Sibbe variety shows a good sorting with grain dimension of about 100µm. The grains, subangular in shape, are constituted mainly by sparitic calcite (shell fragments and skeletons of sea organisms) and secondarily by micritic calcite. There are also rare silicatic grains. The

binder is scarce and constituted by sparitic calcite. The porosity is high ( $\approx 50\%$ ) and mainly constituted by macroporosity (most of all pores have a diameter  $\approx 48\mu\text{m}$ ). The petrographic classification is grainstone and intrasparite. The decay of historic stone develops mainly through the detachment of the crust.

**Table 1.** Physical characteristics of Maastricht limestone

Stone	Water absorption by immersion	Water absorption coefficient	Bulk density	Open porosity	Main pore diameter
	% wt.	$\text{kg/m}^2\text{min}^{1/2}$	$\text{g/cm}^3$	% vol.	$\mu\text{m}$
Maastricht limestone	34,4	20,2	1,3	50	48

#### **4. Application procedure**

Stone specimens were conditioned in the laboratory before the experiment. The treatment was performed on  $5 \times 5 \times 3 \text{cm}^3$  prismatic specimens and only one face of the specimen was treated with a certain volume of the product (30ml). The product was applied by syringe pouring the stone surface until the total volume of 30 ml of the product has been soaked. The volume (30ml) was chosen as a result of a preliminary test when the amount of the product needed for the wetting of  $75 \text{cm}^3$  ( $5 \times 5 \times 3 \text{cm}^3$ ) stone specimen had been determined. The selected volume (30ml) 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 darkening of the impregnated stone material) reaches the bottom of the stone specimen. The time needed for the first and for the successive applications (2-6) was measured.

Specimens for the bending test, US and porosity investigated in depth profile were treated on the face  $5 \times 3 \text{cm}^2$ . 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 4 days. This time was sufficient for drying out of impregnated stone under the laboratory condition which had been found on the basis of an individual preliminary test. Stone specimens were not covered by any impermeable coating which should control 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 alcohol medium of the nanolime and also to a high and large stone porosity. Stone specimens were able to absorb 30ml 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 ( $5 \times 5 \times 3 \text{cm}^3$ ). These specimens were impregnated by the same manner like the previous specimens with one difference that the product was applied through the face  $5 \times 5 \text{cm}^2$  to the depth of 3 cm.

The maturing of impregnated stone specimens occurred in dry conditions (laboratory environment,  $20\text{-}25^\circ\text{C}$ ,  $30\text{-}40\%$  RH) without any special care. The testing of impregnated specimens started one month after the consolidation treatment.

The stone specimens were analysed with several techniques in the following order: propagation of US velocity, bending test and open porosity distribution by MIP - all in the depth profile, and water accessible porosity and compressive strength.

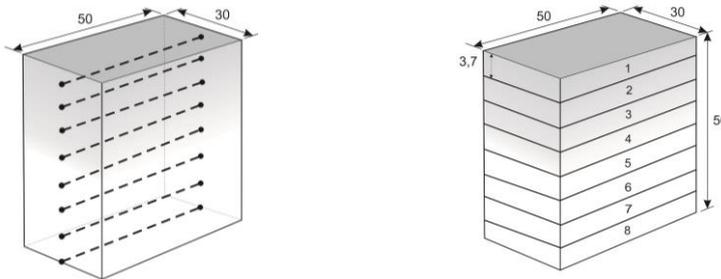
Results from the performed tests are expressed as an average value gained from individual measurements of two specimens treated with the same procedure.

## 5. Methods

The US velocity was measured with a portable instrument USG 20 (Krompholz Geotron Elektronik, FRG) 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 a first step, the untreated stone specimens were measured in all three spatial directions (one measurement for the one axis) so that the difference between X, Y and Z axes was found for each specimen and an 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 1.a). 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.

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 to slices and so 8 rectangular thin plates of the depth  $3,7\text{mm} \pm 3\text{mm}$  with the top side parallel to surface were created (Figure 1.b). Slides were marked 1 to 8 and their specific positions relating the original surface were registered. 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 to determine 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 laboratory (20-25°C /RH 30-40%) using load cell Lucas 100 kN for the load measurement, LVDT 1 mm sensor for the deflection measurement, at the cross head speed of 0,15mm/min.

Even tough the destructive character of this method 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.



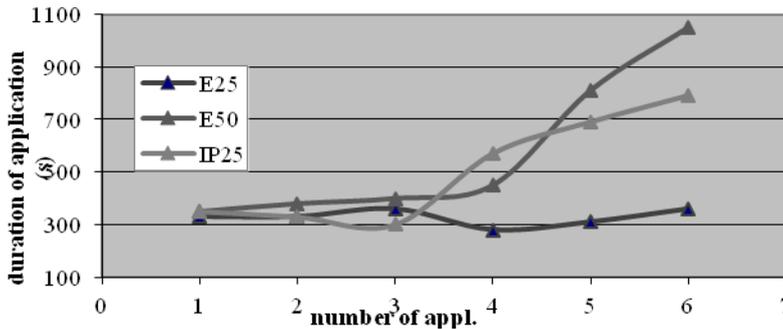
**Figure 1. a (left)** Layout of the US velocity measurements from top to bottom, **b (right)** Layout of a specimen cutting to slices for detailed bending strength tests.

The open porosity and its distribution in the studied materials were determined by Mercury intrusion porosity, using a Quantachrome porosimeter, model Poremaster PM-60-13 with pressure range of 0,005 – 413 MPa. The mercury parameters were set to values of 480 erg/cm<sup>2</sup> 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<sup>3</sup> 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 50x50x30 mm<sup>3</sup> (treated surface 50x50mm<sup>2</sup>). The determination of the porosity accessible to water was carried out following RILEM recommendation (25-PEM norm 1980). The compressive strength was tested on the same specimens like hydric characteristics using load gauge Lucas 50 kN, sensor Megatron 25mm, load speed 0,45mm/min.

## 6. Results and Discussion

The time needed for the first and for the each successive application (2-6) indicates a possible change of transport characteristics of the CaLoSiL within the stone in case of the 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 the top to the bottom for the first and for the following applications. Simple measurement showed that even in case of the 6<sup>th</sup> application the penetration coefficient of this product did not change significantly. Figure 2 illustrates that a different behaviour was found for CaLoSiL IP 25 and E 50. After the first three applications the time needed for specimens impregnation increased as the product penetration ability got worse especially in case of the highly concentrated CaLoSiL E 50. The accumulation of these products in some parts of the stone specimen is probable the reason for the rise of the penetration time in cases of the 4<sup>th</sup> to the 6<sup>th</sup> application.



**Figure 2.** Times needed for wetting of a stone specimen with 30 ml of CaLoSiL in relation to the successive number of application.

The determination of the ultrasonic (US) velocity profiles seems to be a suitable tool for the estimation how an even or uneven distribution of the product's effective compound (calcium carbonate in this case) has developed within the stone specimen after the treatment. The US velocity in the untreated specimens was 1.7-1.8 km/s and the profile was quite homogenous (Figure 3). Most of the treated specimens showed an increased velocity in the surface area (top and bottom), probably as a result of the cumulation of the consolidation product during the evaporation period.

The increased US velocity in the bottom region gives an evidence that products penetrated the all depth of the specimen (5 cm). The rise of US velocity 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 2 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 US velocity measurements that multiple applications of the CaLoSiL products lead to cumulation of the product within the surface region and this trend is more significant in case of the higher concentrated studied type - CaLoSiL E 50. The optimal procedure for consolidation of the investigated stone seems to be 2 applications of the lower concentrated types - CaLoSiL E 25 or IP 25. Different behavior of the products E 25 and IP 25 has not been found in case of the US velocity tests: the differences between the velocity profiles are quite low for the both products with a different alcohol medium.

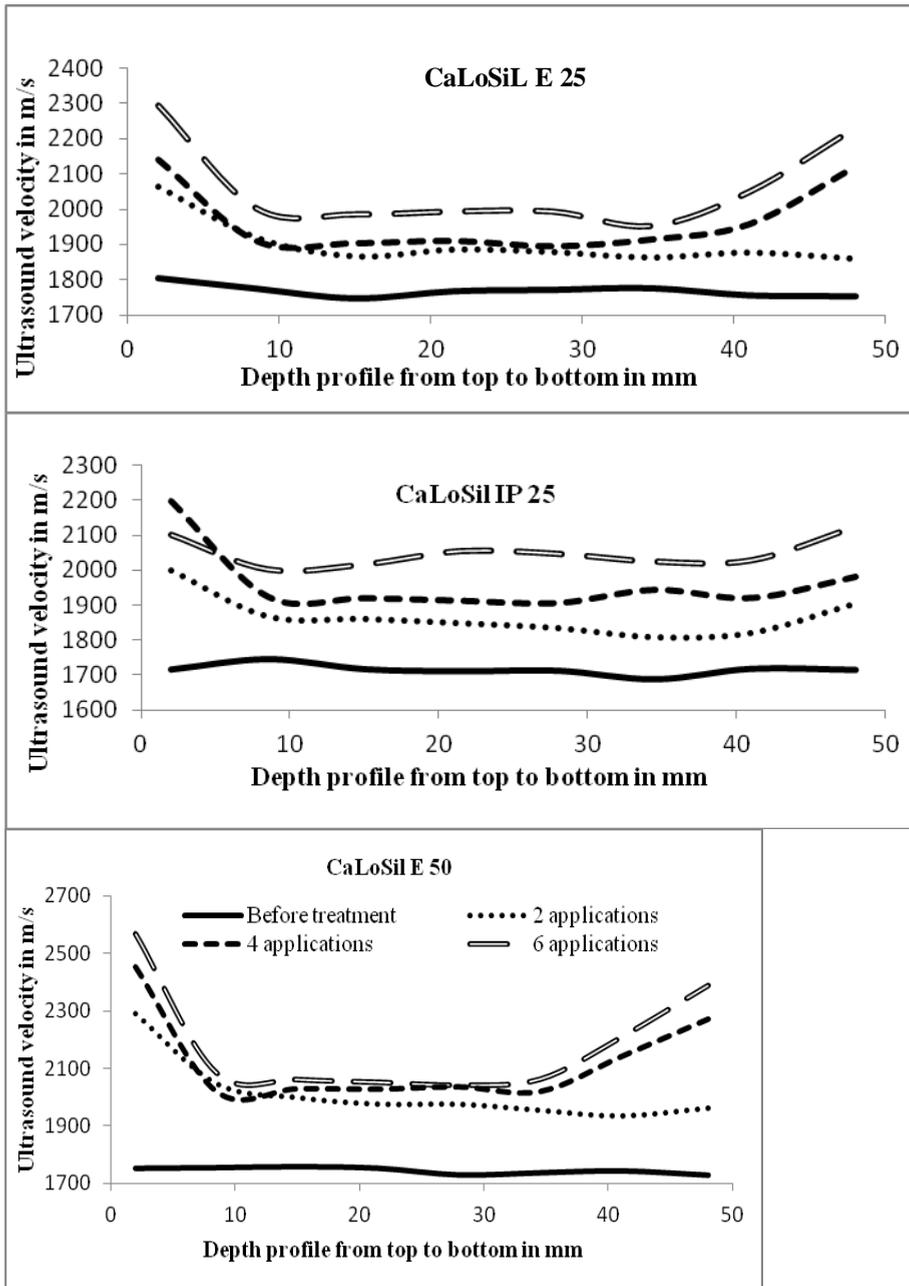
The US velocity corresponds with the stone modulus of elasticity and characterizes its change resulting from the consolidating treatment very sensitively. Bending strength profiles (Figure 4) brought similar results but in detail these data have a higher scatter, which is probably influenced by local defects. Considering the distribution of the strength in the profile the better results were found on stone consolidated by 2 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.

The strength rise considering overall stone specimens is illustrated in Figure 5 for both the bending and the compressive strengths. The distribution of the strength in the stone specimen profile is not considered in these graphs: the average values of the

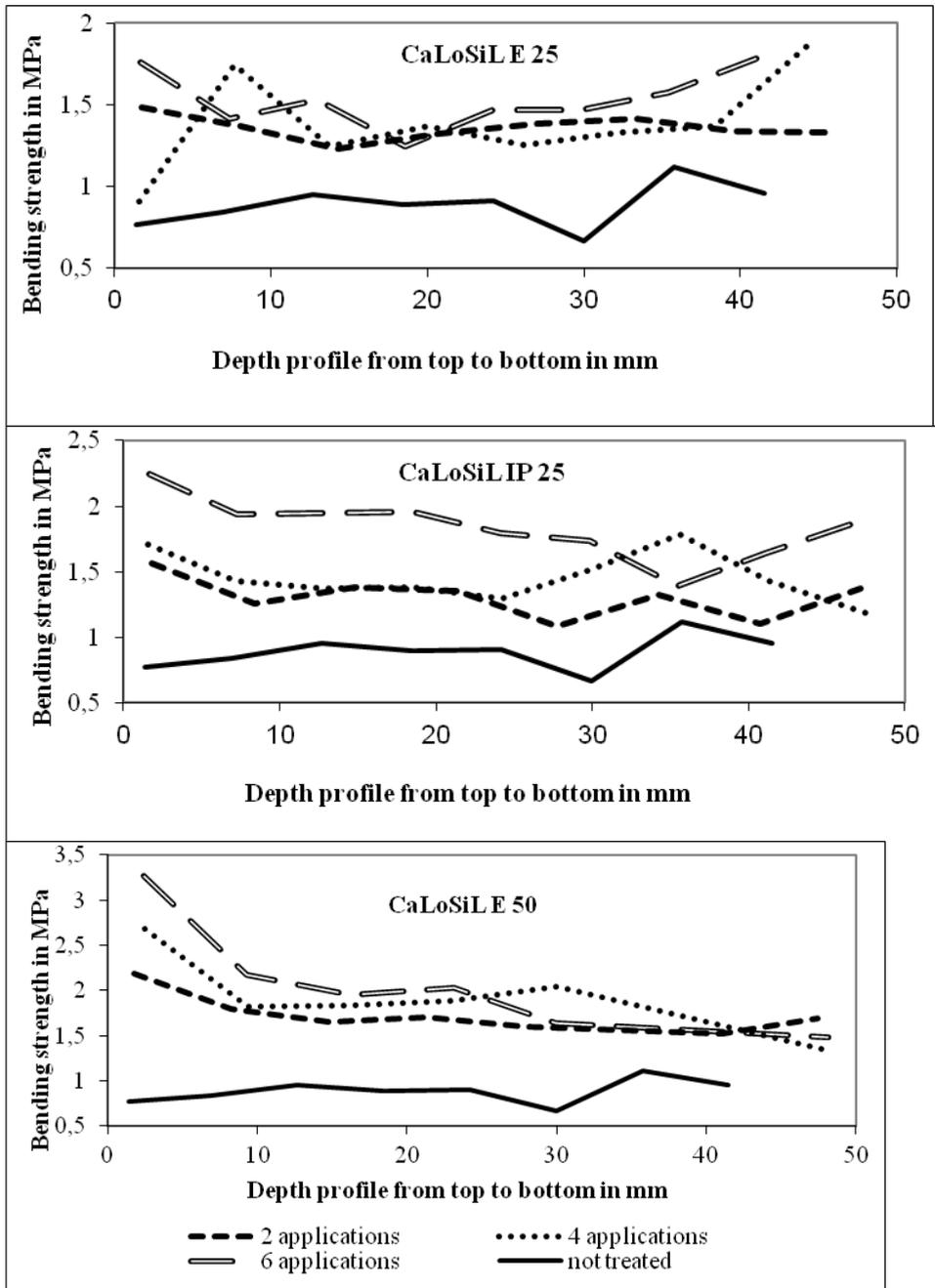
specimen strength are shown (for the bending the average is calculated from individual slices strength of 2 specimens and the compressive strengths were determined by testing 2 specimens  $5 \times 5 \times 3 \text{ cm}^3$ ). The increase of the average bending strength value of a specimen represented 45% after 6 applications for E 25, 63% for IP 25, and 100% for E 50. The rise of the compressive strength was 93% for E25, 47% for IP 25, and 126 % for E 50 after 6 applications. After 2 applications (which seems to be a suitable treatment amount relating the even distribution of the product in the stone) the bending strength increase represented 20% (E 25), 18% (IP 25) resp. 54% (E 50) and the compressive strength increase 50 % (E 25), 23% (IP 25) resp. 73% (E 50). The presented test results support conclusions that two applications of the CaLoSiL products seem to be the optimal procedure for the treatment of porous limestone. When a stronger strengthening is needed the higher concentrated product E 50 applied with care may be useful.

The porosity investigations correspond with previous results. The values of the open porosity obtained on specimen  $5 \times 5 \times 3 \text{ cm}^3$  were quite optimistic: the porosity decreased due to the treatment (table 2) but not dramatically. MIP method used for the testing of porosity in the depth profile showed its uneven distribution coming from a bigger influence on pores near the surface (Figure 6) even after 2 applications.

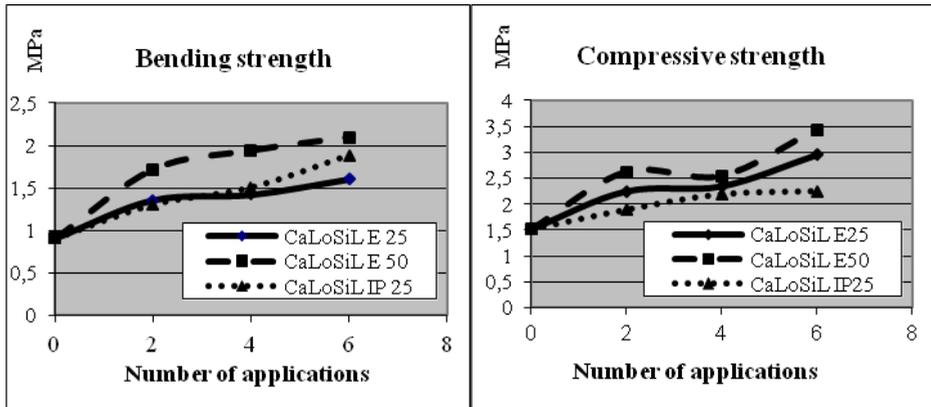
Concerned the stone color the local white hazes appeared on the surface of some specimens (IP 25 and E 50 after 6 applications of the products). White staining was not found for specimens treated with the CaLoSiL E 25.



**Figure 3.** Ultrasound velocity in depth profile for the Maastricht limestone before and after treatment with CaLoSiL IP 25, CaLoSiL E25 and CaLoSiL E 50.



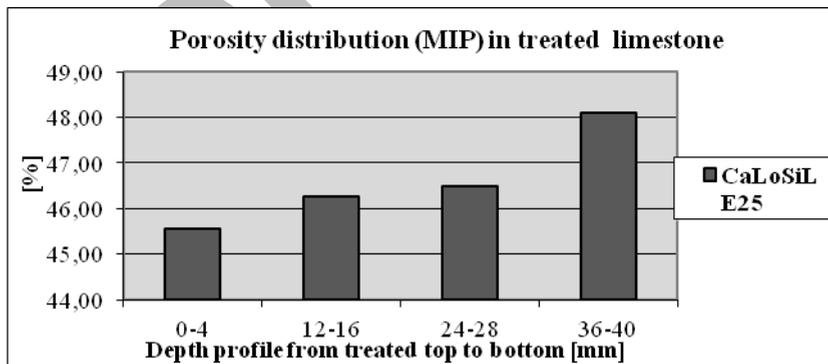
**Figure 4.** Bending strength of stone slices in the depth profiles for not treated specimens and the specimens treated with CaLoSiL E 25, CaLoSiL IP 25 and CaLoSiL E 50.



**Figure 5.** Increase of bending strengths (left graph) and compressive strengths (right graph) of the Maastricht limestone due to consolidation with multiply applied the CaLoSiL products.

**Table 2.** Reduction of water accessible porosity of the Maastricht limestone due to consolidation with 6 applications of the CaLoSiL products

Maastricht limestone	Water accessible porosity (RILEM I/1) %	Decrease of porosity	
		% abs.	% rel.
untreated	50,3		
treated by 6 cycles E 25	47,4	2,9	5,8
treated by 6 cycles IP 25	47,4	2,9	5,8



**Figure 6.** Distribution of open porosity values (MIP) within the treated specimen depth profile (CaLoSiL E 25, 2 applications).

## 7. Conclusions

The appropriate amount of the product (both the concentration of the effective compound and the sum of applications) has to be chosen in relation to the stone porosity

and the treatment condition in order to achieve the regular distribution of the product in the substrate. The optimal procedure for consolidation of investigated stone seems to be 2 applications of the lower concentrated types CaLoSiL E 25 or IP 25. Application of the products with a different alcohol medium (CaLoSiL E 25 and IP 25) generates rather low observed differences measured by the US velocity and the strength in the depth profiles. The higher sum of performed applications resulted in an uneven distribution of the product in the stone specimen which was followed by the increase of the strength in the surface part. The local white hazes appeared on the surface of some stone specimens after 6 applications of the products IP 25 and E 50.

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