TEOS AND TIME: THE INFLUENCE OF APPLICATION SCHEDULES ON THE EFFECTIVENESS OF ETHYL SILICATE BASED CONSOLIDANTS

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ABSTRACT

An investigation was carried out at KIK-IRPA on the application modalities of ethyl silicate based products aiming at understanding the influence of time between successive applications on the pore structure and on the final strengthening effect of stones. Samples of Maastrichter lime stone were treated with different formulations and dilutions. The number of treatments varied from one to three with an interval between successive treatments ranging from one day to three weeks. Mercury porosity measurements, polymerized product content and hardness profiles obtained by a drilling resistance measurement system (DRMS) were used to evaluate the consolidating properties. Noticeable differences in pore blocking and in overall hardness were observed in samples that were treated at one day intervals and those treated at three week intervals. The strengthening effect also seems to vary with the type of formulation.

KEY WORDS:

Consolidant, ethyl silicate, application schedule, pore structure, DRMS

1. INTRODUCTION

Of the many difficulties present during the restoration of historical buildings, certainly the consolidation of surfaces is one of the most challenging: it involves in depth irreversible treatments, whose positive outcome is not readily visible, and whose efficiency is rarely monitored on a long term basis. Many different products have been used over the past century, but the consolidant that best seems to be standing the test of time in terms of efficiency, durability and lack of side effects on damaged historical masonry, is ethyl silicate (tetraethoxysilane or TEOS)[1]. Its vast current use is also due to its easy application and versatility, for it has proven efficient on lime stone, sandstone and brick masonry[2]. Though commonly used, the instructions given by manufacturers regarding the number of applications and the time lapse necessary between treatments is often missing or contradictory.

The aim of this investigation is thus to evaluate the effects of repeated applications at different time intervals of a common ethyl silicate formulation available on the European market on lime stone samples. One of the consolidants tested has a new catalyst formulation, and is not at present commercially available.

The often missing link between practitioners (restorers) in search of answers on which consolidant will perform best and how to apply it, and researchers who wish to give sound advice, lies in the necessity of systematically introducing the use of convenient in situ methods of control and evaluation of consolidation treatments. For this reason this study has included drill resistance measurements using a drill resistance measurement (DRMS) device[3]. The DRMS technique was developed as a movable analytical tool especially for use directly on buildings. It has proven to be a practical and valuable tool for on site evaluation, for it provides a hardness profile of the stone, running up to five centimetres deep, hence allowing an evaluation of the alteration degree and depth before, and the effect and degree of penetration of the product after treatment.

Porosimetric properties were measured by mercury intrusion porosimetry (MIP). This technique allows the evaluation of the influence of the consolidation on the total porosity and on the pore structure of the sample, hence on the distribution of the polymerized product amongst the pores, in relation to the application schedule.

2. EXPERIMENTAL

2.1 Products

Three formulations were tested:

A) Tegovakon® V 100 (Degussa) in a 70% solution of white spirit (dry weight 38,20± 0,08 %)
B) Tegovakon® V 100 (Degussa) (dry weight 52,75± 0,06 %)
C) CPX309 (Degussa) (dry weight 55,90± 0,19 %)

The dry weight is determined by weighing 0,5 g of product before and after one week of conditioning at 20°C and 55% RH. The values determined are the average of three measurements.

2.2 Substrate

Maastrichter lime stone was chosen as a substrate for this study. It is a pale yellow biogenic lime stone quarried between Belgium and the Netherlands, used as a building stone in romanesque and gothic monuments mainly in the province of Limburg. The quarried stone we have used has a lime content between 90 and 96%, a density of 1,37 ± 0,01 $g \cdot cm^{-3}$ and a total porosity measured by MIP between 47 and 48%.

2.3 Treatment

Samples of Maastrichter stone cut into cubes with sides of five centimetres were treated with each of the three products by capillary absorption, on one face, until the product reached the height of 1,5 cm. They were weighed before and after each treatment in order to calculate the quantity of product absorbed, then placed treated side up.

Each product was applied, once, twice and three times, at four different time intervals: one day (a), four days (b), one week (c) and at a combination of two and three weeks (d). Hygrometric conditions at application were 22°C and 40% RH. Samples were stored at the same conditions for one month after the last treatment, in order to allow complete polymerization of the ethyl silicate.

2.4 Evaluation of the treatment

2.4.1 Product uptake and SiO_2 content

The uptake of product after each individual application was determined by weighing the sample before and after treatment. The samples were weighed again after one month in order to determine the amount of ethyl silicate that has polymerized to SiO_2 inside the stone.

2.4.2 Mercury Intrusion Porosimetry

Mercury intrusion porosimetry (Autopore II 9220, Micrometrics) was performed on the untreated stone and on samples taken from the treated face of the stone cubes, one month after the last treatment. Total porosity values and pore size distribution results were used to examine the different behaviour of the products applied according to different time schedules.

2.4.3 DRMS

Samples were drilled three times with a DRMS device (DRMS cordless 3.04, SINT Technology) to a depth of 4,5 cm, with a revolution speed of 100 rpm and a penetration rate of 20 $mm \cdot min^{-1}$. This device measures drilling resistance in force (N).

3. RESULTS AND DISCUSSION

3.1 Product consumption

From the data relative to the quantity of product absorbed after each treatment, it has clearly emerged that the greater the number of treatments performed on any one sample, the lower the product consumption will be. This is especially true for treatments with the pure products B and C. As the time between treatments increases, this decrease tends to become less evident, meaning that the greater the time in between treatments, the more product can be absorbed by the substrate.

3.2 Total porosity and SiO_2 content

Figures 1 and 2 summarize the total porosity values obtained for samples treated twice and three times at the four different time intervals. After two treatments (figure 1) almost no effect of the time schedule on the total porosity was observed. In the case of three treatments (figure 2), with the exception of the seven day interval, the total porosity tends to decrease as the time in between two treatments increases for the pure products B and C. The results are more or less in accordance to the reduction in consumption and to the increase in weight (of SiO_2) of each sample. As expected the diluted product A gave the smallest total porosity reductions.

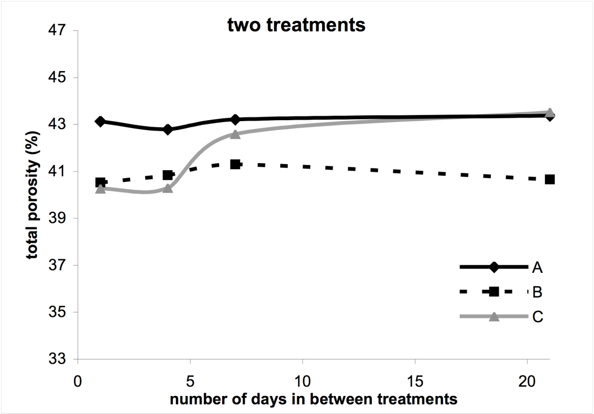

figure 1: total porosity of Maastrichter stone treated twice at different intervals.

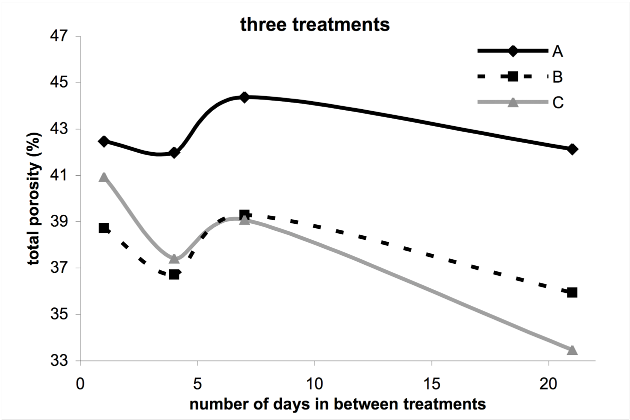

figure 2: total porosity of Maastrichter stone treated three times at different intervals.

3.3 Pore size distribution

3.3.1 General

Mercury porosimetry measures were examined to understand how the consolidant was modifying the sample's pore structure after each treatment. Figure 3 is an example of how the cumulative pore size distribution changes as samples are treated once, twice or three times.

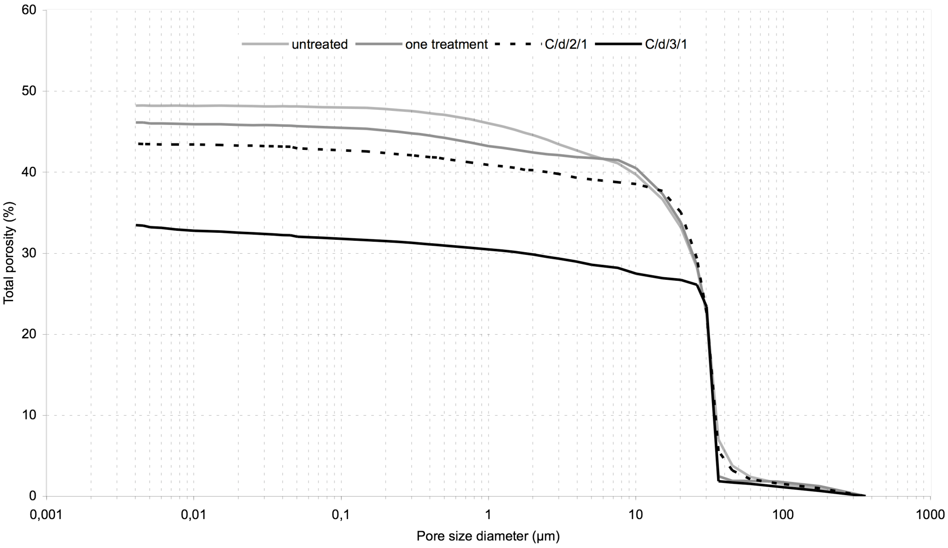

figure 3: Cumulative pore size distribution of untreated Maastrichter stone (light grey) and after one (grey), two (dotted) and three (black) applications with product C. The time in between successive treatments was three weeks.

In order to better recognize the variations that occur in the pore size distribution, the changes in the absolute volume of each pore with a specific size can be presented graphically as the difference between the volume of the pores of the treated sample and that of the untreated sample (cumulative effect), or that of a sample having one less treatment (individual effect). Where the plotted values are negative, there is a reduction of the volume of those pores compared to those of the sample they are referred to. When a reduction of pores of a certain diameter is accompanied by an increase of the number of pores having a smaller diameter, this means that those pores have been reduced in size. If negative values are not accompanied by positive ones in the region of a smaller pore size, it means that the pores corresponding to the diameter of the negative values have been blocked and not reduced in size.

3.3.2 Effect of the first treatment on the pore size distribution

The untreated Maastrichter stone is a macro porous stone having around 30% of pores with a diameter between 20 and 36 µm (figure 3). As illustrated in figure 4, the first consolidation results in a reduction of the pores of 36 µm in favour of pores of 30 µm in diameter for all three products. Pores with a diameter smaller than 10 µm are instead blocked. For products B and C the blocking occurs mainly in pores of diameters between 7,6 and below 4,9 µm, whereas for product A it is pores smaller than 3 µm that are blocked.

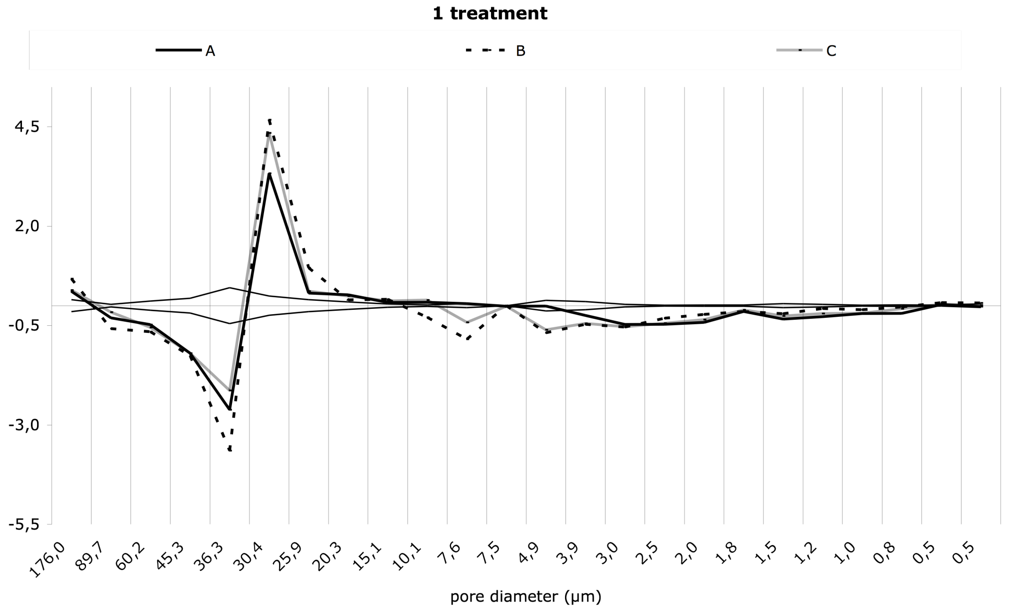

figure 4:
effect of the first treatment on the pore size distribution for product A (black), B (dotted) and C (grey). The standard deviation obtained from three MIP measurements on the untreated stone is marked by a thin black line.

3.3.3 Effect of successive treatments on the pore size distribution

As more treatments are performed on the samples the pore blocking is intensified for all three products and characterized by a shift towards bigger pores. Figure 5 illustrates the cumulative effect on the pore size distribution of a second treatment with products A, B, and C applied after four days. The undiluted products B and C show an increase in the quantity of pores blocked between 15 and 10 µm. Product A is instead blocking pores at 7,6 µm and at diameters inferior to 5 µm. A third treatment, again applied after four days, is increasing the pore blocking in diameters up to 26 µm for products B and C, whereas product A results in an increase of blocking in 10 µm pores (figure 6).

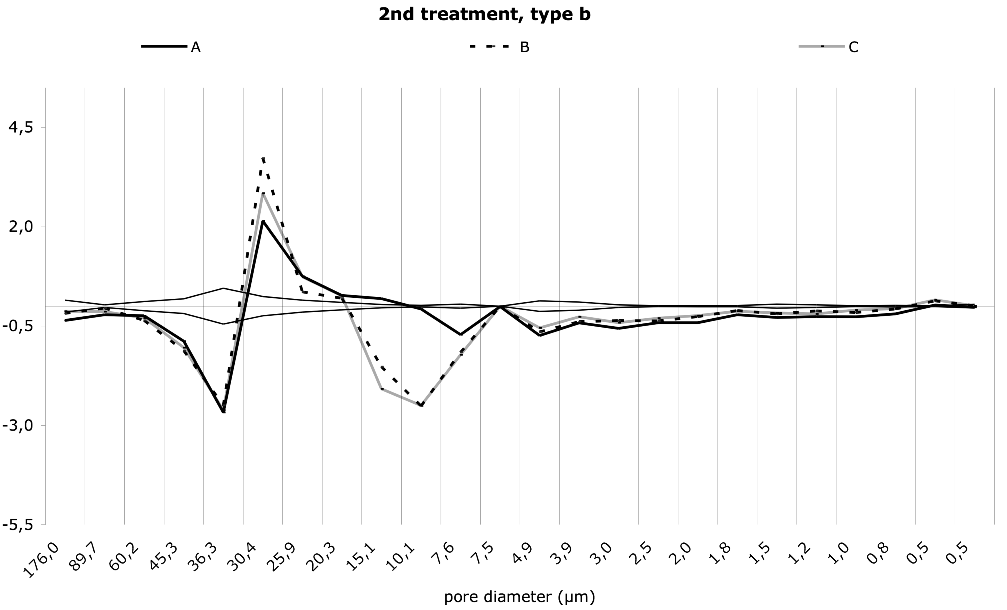

figure 5: cumulative effect on the pore size distribution of two treatments with products A, B, and C, applied after four days.

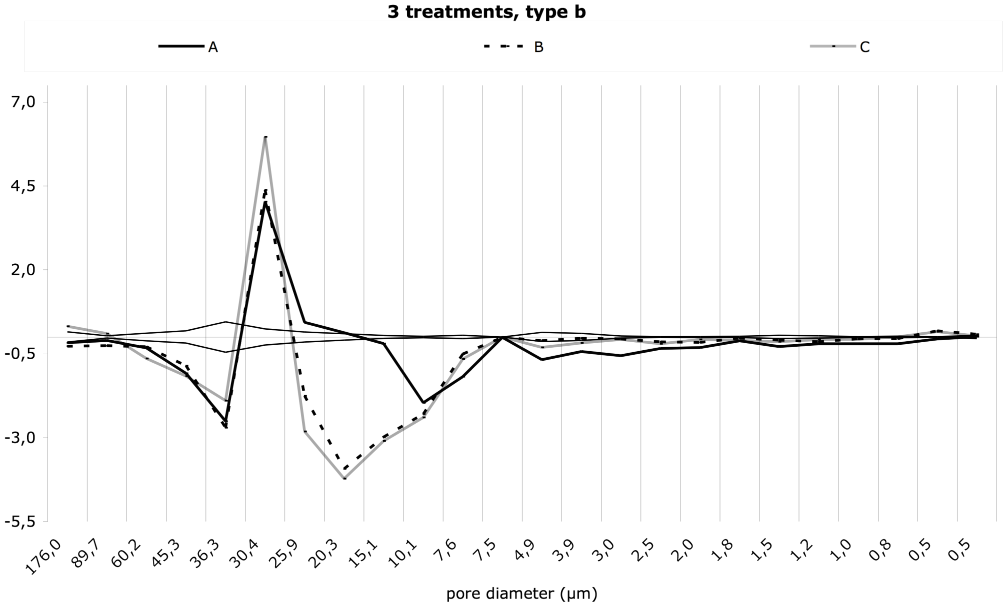

figure 6: cumulative effect on the pore size distribution of three treatments with products A, B, and C, applied with a four day interval.

In order to evaluate the influence of the application schedule on the pore size distribution, all samples treated twice or three times with the same product were compared. Figures 7 and 8 show the variations of the pore distribution for samples treated twice with product A (diluted). Figure 7 represents the individual effect of the second treatment. Pores in the range of 7,6 -10 µm of samples treated at the one day schedule show the greatest pore blocking. This is confirmed in figure 8, where the cumulative effect on the pore size distribution of samples treated twice with product A reveals the greatest pore blocking in the case of the one day interval.

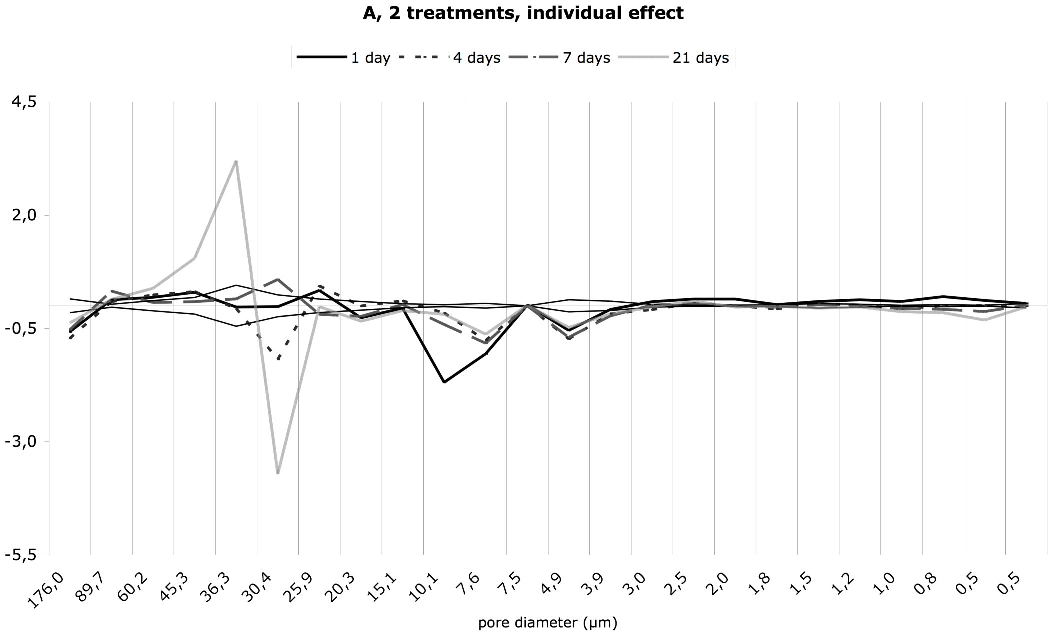

figure 7: individual effect on the pore size distribution of the second application of product A at four different time intervals.

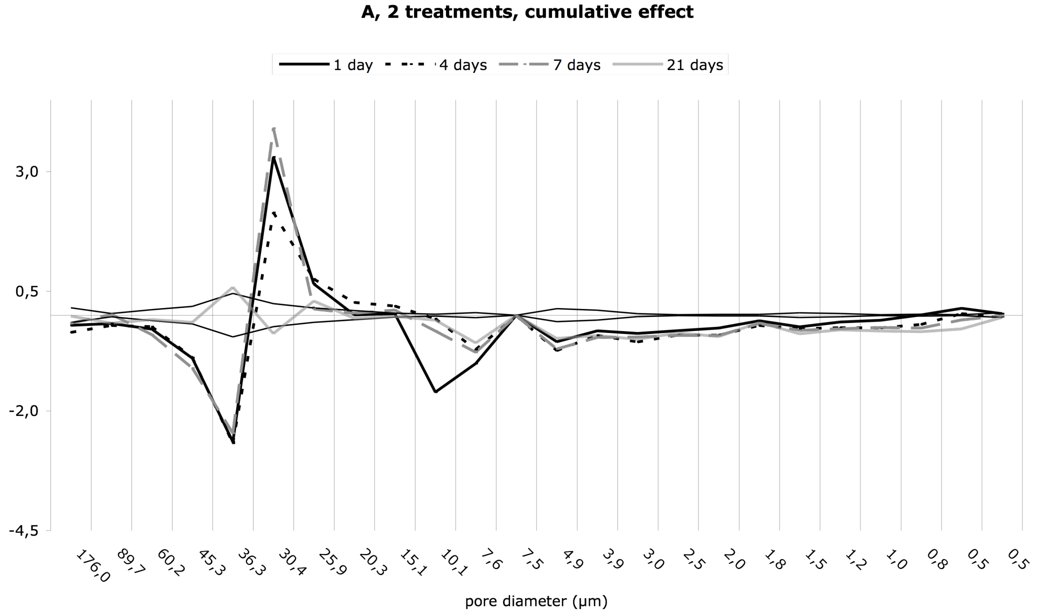

figure 8: cumulative effect on the pore size distribution of two applications of product A at four different time intervals.

A third treatment with product A results in a further increase of pore blocking, but the only schedule that results in blocking of the 20 µm pores is the one day timing.

As for product C, in figure 9 the cumulative effect of three treatments on the pore size distribution is illustrated. There seem to be no relevant differences in pore blocking amongst the four treatment schedules. Its behaviour is much similar to that of the other pure product B.

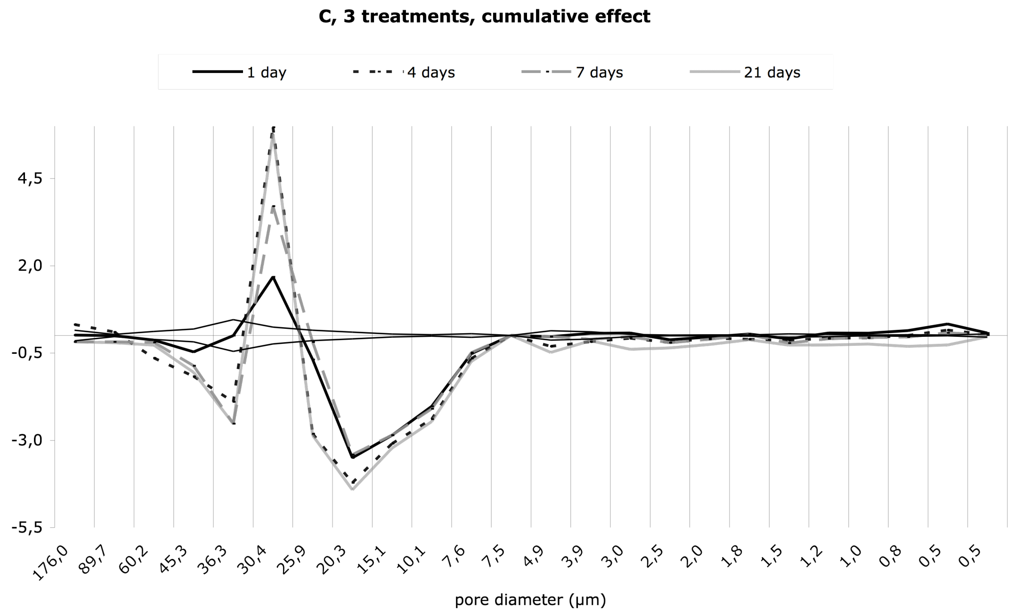

figure 9: cumulative effect on the pore size distribution of three applications of product C at four different time intervals.

3.4 DRMS

All samples showed an increase in drill resistance after treatment. Values reported in figures 10 and 11 are expressed as a percentage increase in strength compared to the average drill resistance of the untreated stone, respectively for samples treated twice and three times. As it could be expected the lowest strengthening was obtained for the diluted A product; the highest values were obtained for product B. Especially in the case of three treatments, there is an evident increase in the overall strength as the time between treatments increases. No direct correlation between the reduction in total porosity and the strengthening effect could be observed.

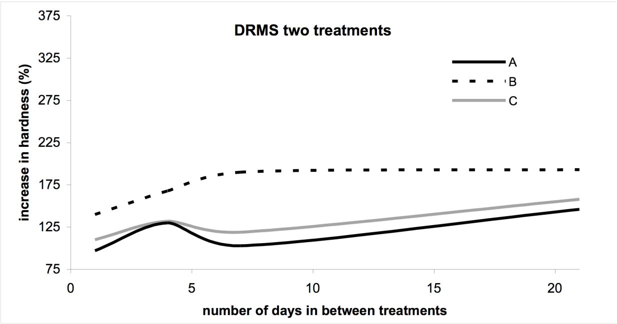

figure 10: percentage increase of the average drilling resistance force for samples treated twice.

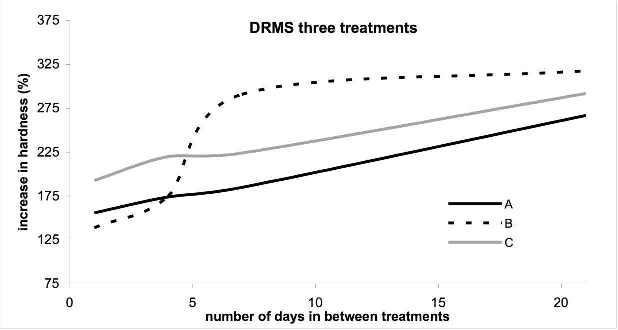

figure 11: percentage increase of the average drilling resistance force for samples treated three times.

The same drilling measurements correlated to the gain in weight of SiO_2 of each sample have revealed some surprising issues. One would expect an increase in hardness for a greater amount of deposited SiO_2. Samples treated two or three times with the same product all have comparable increases in weight yet their drill resistance values increase as the time in between applications increases (figures 12 and 13). Of the three formulations, product B gives the highest strength increase, even compared to the other pure product C, that with similar SiO_2 content gives lower strengthening. This difference may be due to the fact that product C contains a different catalyst, that may induce the formation of more linear structures in the SiO_2 gel, as opposed to the cross-linked structure that the traditional catalyst (dibutyltindilaurate) contained in product B is known to yield[4].

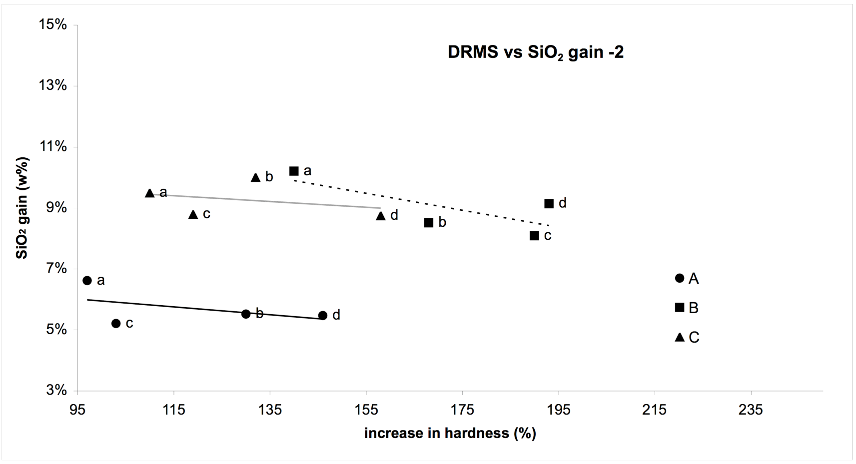

figure 12:
average increase in hardness measured with the DRMS related to the gain in SiO_2 for samples treated twice with products A, B and C at a one day (a), four day (b), one week (c) and three week (d) interval.

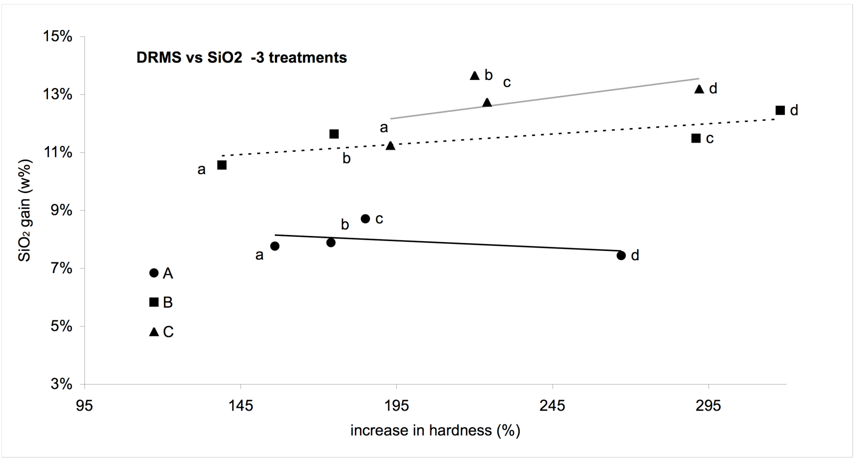

figure 13:
average increase in hardness measured with the DRMS related to the gain in SiO_2 for samples treated three times with products A, B and C at a one day (a), four day (b), one week (c) and three week (d) interval.

4. CONCLUSION

The quantity of ethyl silicate based formulation that has been absorbed by samples of Maastrichter stone in successive treatments increases as the time in between treatments increases. Therefore a longer schedule will favour the penetration of a greater amount of product in the stone. The total porosity of the samples decreases accordingly as the scheduling of the treatments increases over time, especially after a third treatment.

The effect of the consolidation treatments on the pore size distribution has shown a greater blocking of pores for the pure products B and C than for the diluted product A. As the number of treatments increases, so does the blocking of pores of a progressively larger size. For pure products B and C this phenomenon is not affected greatly by the application schedule. The pore blocking caused by the diluted product A is instead highly influenced by time: greater blocking is obtained when the product is applied at one day intervals, rather than at intervals of at least four days.

The strengthening effect of the consolidation treatments measured by DRMS increased as the time in between treatments increased. However there is no direct correlation of this tendency with values of total porosity and of SiO_2 content. A new catalyst contained may be responsible for the lower DRMS values obtained for product C compared to samples containing the same weight in SiO_2 but treated with product B.

5. REFERENCES

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