CONSOLIDATION OF A POROUS LIMESTONE WITH NANOLIME

Dória Costa[1], José Delgado Rodrigues[2]

[1] *Laboratório Nacional de Engenharia Civil, Lisbon, Portugal; drcosta@lnec.pt*
[2] *Laboratório Nacional de Engenharia Civil, Lisbon, Portugal; delgado@lnec.pt*

Abstract

This communication work reports the laboratory experiments with a nanolime product applied to the highly porous limestone currently used in Portuguese architectural heritage. The tests aimed at evaluating the short-term efficacy of the product to induce a mass consolidation effect. Other substrates were also tested for comparative purposes, namely a limestone with a different pore size distribution and a weak lime mortar.

We concluded that the product has a low capability to impregnate these materials. In all cases, although at different levels, a selective migration of the product was verified, as well as an accumulation of the nanoparticles at the surface in contact with the colloidal suspension.

The consolidating agent was not able to penetrate and no consolidation effect was detected in Ançã stone. On the contrary, on the two other materials, some effect could be quantified, despite the low quantity of consolidant deposited in the pores.

Besides the relevant information on the potential capability to consolidate those specific substrates, the work demonstrates the advantage of using drilling resistance to evaluate the consolidation action, not only on soft and homogeneous materials but also on heterogeneous ones. In this particular case, the impregnation kinetics determined with capillary absorption tests gives a misleading information of the real performance as a consolidant. Water transfer properties and the pore size distribution were slightly changed after consolidation and require further investigation.

Keywords: limestone, inorganic consolidation, nanolime colloidal suspensions

1. Why to use inorganic products to consolidate Ançã stone?

Ançã stone was used since ancient times in architecture and sculpture in Portugal. The extreme softness and homogeneity of this material made it possible to produce beautiful sculpted and carved surfaces that are exposed to indoor and outdoor environmental conditions. Despite the characteristics that enabled its widespread use over time, this variety of limestone is a very porous material with low mechanical strength and an undeniable susceptibility to salt damage.

Extremely decayed surfaces are present in several Portuguese monuments and consolidation action has to be considered during conservation interventions. For all these reasons, this variety of stone has been studied since long ago, looking for the most adequate consolidation treatments [Castro 1990; Delgado Rodrigues 1997; 2001].

The choice of an effective consolidant for carbonate stones is a general key goal in cultural heritage conservation including the particular case of Ançã stone. In the stone surfaces where high rates of mass loss are identified, consolidation is intended to slow

Copyright transfered

down or stop erosion, also attempting to restore the mechanical characteristics of the stone when it was originally placed in the monument.

In general terms, it can be considered that the main types of consolidants used in practice for strengthening carbonate stones are silicate-based products and resins, (namely acrylics) but sometimes very fluid epoxies may also be necessary, in particular if structural demands are involved. The discussion of the advantages and drawbacks of these solutions are out of the scope of this work. However, it is important to highlight that although they have a unique ability to penetrate into the stone, at present the ethyl silicate-based products are not considered a good solution for consolidating pure carbonate stones, not only due to chemical incompatibility with the substrate but also to the lack of chemical bonding between the product and the substrate. The surfaces of carbonate grains do not have the capability to react with the consolidant and the action of silica gel formed after polymerization is assumed to be simply that of a compacting agent, acting as filler of the stone voids. This limitation was pointed out in the early 90's [Danehey 1992, Wheeler 1992] and since then several remedial solutions were proposed to solve this drawback, changing the composition of the ethyl silicate or adding coupling agents to facilitate the chemical bonding of the product with the stone substrate. Some studies on Ançã stone were also done [Pamplona 2008, Pinto 2008] but as far as we know and up to now, the success of these solutions is still controversial.

In this context, inorganic consolidation is considered particularly relevant. In fact, inorganic consolidants were used in the past but in the last years new perspectives of their use have been brought up [Hansen 2000] and some practical work, including in this stone type was done [Bracci 2008]. Among others, one possible solution is to use lime-based consolidants; in the case of lime water, $Ca(OH)_2$ reacts with atmospheric carbonic dioxide and calcium carbonate is produced. The great advantage of using this solution is the total chemical compatibility with the calcitic substrate, allowing the bonding of stone grains to strengthen stone. In spite of the chemical compatibility, lime-based treatments were considered to have some limitations, such as the reduced impregnation depth and the very slow rate of conversion of calcium hydroxide into calcium carbonate.

2. Brief overview of calcium hydroxide nanoparticles colloids with potential use as consolidants

Nanolime suspensions now available in the market are very promising and are considered to have high penetration capability, and able to consolidate not only very porous mortars but also porous stones.

Specially designed in Europe for the use in Conservation, CaLoSiL® is a trade brand that produces nanoparticles of lime hydrate stabilized in different type of alcohols (ethanol, iso-propanol or n-propanol). For consolidation purposes, typical concentrations are between 5 and 50 gram/liter (CaLoSil 5, CaLoSil 25 and CaLoSil 50). According to the producer, the average particle size of the nanoparticles is 150 nm. However, different formulations of the same brand including nanolime particles and silicic acid esters are under research in the framework of the European project “Stonecore”, still in progress.

CaLoSil products are “ready to use” but can be diluted. Multiple and successive applications are usually recommended but the number is dependent on the characteristics of the substrate, taking into consideration the objective of the treatment.

Copyright transfer

According to literature, the most current application method of the product is by brushing although others methods are indicated by the producer as appropriate.

It must also be mentioned that one of the first tentatives to synthesize $Ca(OH)_2$ nanoparticles stable dispersions was performed in CSGI (Center for Colloid and Surface Science), Italy. Under the commercial name of "Nanorestore®" the product is distributed by CTS (Italy) and has been used in practice to consolidate wall paintings (and also limestone) since 1997.

Several papers on nanolime products applied to different porous materials were also published [Daniele 2008, 2010; Campbell, 2011] concerning not only consolidation but also protection purposes.

3. Objectives, method and materials used in this study

3.1 Objectives

The experimental work performed in the laboratory aimed to evaluate the potential use of suspensions of nanoparticles of calcium hydroxide to consolidate Ançã stone. According to the current procedure performed in our group, also applicable on carbonate stone types [Pinto 2002], this evaluation is a step by step process.

To evaluate the effectiveness of the consolidant two relevant parameters are considered: the impregnation capability of the product and the consolidation action it promotes. In this specific case, the main goal was to achieve a mass consolidation of Ançã stone, without pronounced interfaces between treated and non-treated zones.

Based on the results of the first assessment the next step of research is planned. When considered as successful, other relevant aspects will then be successively evaluated. Otherwise, it may be necessary to clarify the reasons for the performance observed, to change the conditions of application or even to abandon the study of the product if considered totally inappropriate for the purpose.

3.2 Method

In the first phase, two parameters are considered as the most relevant; *i*) the impregnation capability of the product and *ii*) the consolidation effect that results from it.

In what concerns i), it is recommended to apply the product by capillarity and to follow the evolution afterwards (curing process) until all the solvent has been released. Dry mass after consolidation and the quantity of the product absorbed during treatment shall be computed. In some cases, it is particularly useful to compute the absorption coefficient to express the advancing "velocity" of the wet front.

When the product is applied by capillarity, the results overestimate the capability of the product to migrate into the stone, and this fact has to be considered. However, this process is able to give information about the real interaction of the product with the substrate and is highly reproducible. Other influencing factors will be discussed afterwards.

Drilling resistance was the parameter used to quantify the consolidation effect promoted by the treatment (*ii*) and to identify the impregnation depth (*i*).

In this particular case, other characteristics of the material were determined in the consolidated stones in order to evaluate the effectiveness of the treatment. Ultrasonic velocity, water properties (water absorption by capillarity and by sponge contact) and the pore size distribution after consolidation were used as a complementary evaluation of the efficacy of the consolidant.

Copyright transfered

3.3 Stone materials and the consolidation method

Ançã is a yellowish white, very homogeneous and fine grained limestone. It is formed almost exclusively of calcite grains (not less than 95%), with minor amounts of quartz. It is extracted in the Coimbra region (Central Portugal).

Table 1 presents the most relevant physical characteristics of this stone; it is worth mentioning the high values of water absorption, in agreement with the high porosity of the material. Also relevant is the low mechanical resistance, here indicated by the bending strength and hardness (assessed with drilling resistance). Another relevant characteristic is the pore size distribution as seen in Figure 1.

Real density ($kg.m^{-3}$)	2711
Bulk density ($kg.m^{-3}$)	1972
Open porosity (%)	26 - 28
Hg porosity (%)	≈27
Water absorption by capillarity coefficient ($kg.m^{-2}.h^{-0.5}$)	9.9 - 10.9
Water absorption (48h) (%)	12 - 14
Ultrasonic pulse velocity ($m.s^{-1}$)	3000 - 3200
Drilling resistance (N) (at 600rpm;10mm.min^{-1})	2.3 - 4.3
Bending strength (MPa)	3.8 - 4.4

Table 1. Physical properties of Ançã limestone

Taking into account the stone characteristics, it was decided to use CaLoSil 50, in ethanol. As it is clear from the pore size distribution (Figure 1), about 90% of the pores have an access radius larger than the average dimension of the product nanoparticles. Theoretically, only a small percentage is smaller and fully inaccessible (l to the left of the asterisk in the XX axis). Other characteristics of the porous system may be relevant, but the high percentage of pores considered accessible allows us to admit that the product can have access and promote an effective consolidation.

For our specific purposes, the most concentrated version of the product (CaLoSil50) seemed more adequate, as we considered that it is important to significantly improve the stone strength. In this case, one of the great advantages of CaLoSil solutions is to allow a faster consolidation process when compared to the conventional use of limewater, which needs a very large number of applications to be effective (Drdácky 2008).

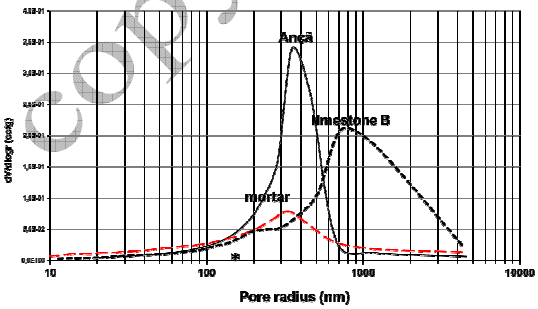


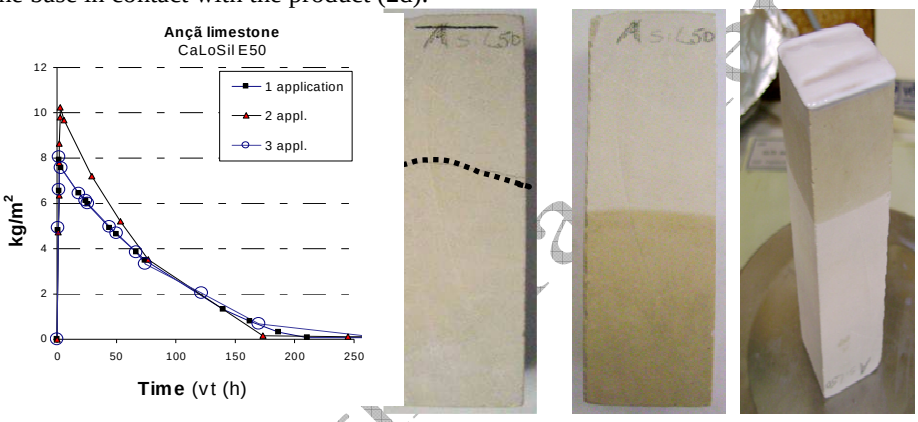
Figure 1. Pore size distributions of the tested materials. The asterisk in the XX axis indicates the average dimension of the CaLoSil particles. The macroporosity was not determined and the pore size distribution in the mortar samples results strongly incomplete in this range.

copyright transfered

4. Results

4.1 First set of experiments: the application of the product on Ançã limestone

Specimens were oven dried (70±1 ºC) and the product was applied by capillarity; the base in contact was immersed about 1cm. From time to time, the absorption process was interrupted, the face in contact with the product cleaned, and the specimen weighed. The end of the test was determined when the height of the liquid front was large enough, which was reached in about 3 to 5 hours in the present case. At the end of the impregnation process, the faces in contact with the product were cleaned with the solvent, in order to remove the excess of product accumulated, which would produce an undesirable rigid layer on those faces. Drying took place in laboratory conditions with the lateral faces protected to avoid a too fast evaporation. The process was repeated three times, in similar conditions. Figure 2a represents the absorption curves obtained, the macroscopic aspect of one specimen after the 1st (2b) and 3rd applications (2c) and the base in contact with the product (2d).



a) Absorption-drying curves. 1st and 3rd applications for 3 hours; the 2nd for 5 hours.

b) After 1st application (dry). The position of the liquid front is indicated

c) After the 3rd application (wet)

d) accumulation of particles at the base of the prism during the 2nd application

Figure 2. Application of CaLoSil E50 on Ançã limestone

During these experiments, it was clear that particles had accumulated at the base of the specimens and a selective migration of the product was hypothesized.

Table 2 contains the most relevant parameters of this application process.

	Absorption dynamics Product absorbed (kg/m²) / liquid front after 3h (cm)
1st application	7.9 / 4.3
2nd application	7.8 / 4.0
3rd application	7.8 / 4.1

Product retained	
Estimated (g)	Measured (g)
0.42	0.02
0.52	0.01
0.43	0.01

Table 2. Absorption dynamics (left) and amount of dry matter retained after treatment (right)

The estimated values of the dry phase were computed after the concentration indicated by the supplier, while the measured values were those actually determined.

copyright

However, when comparing values, it must be realized that the dry matter is calcium carbonate, while the estimated values concern calcium hydroxide. These results indicate that most of the intake product corresponds to the solvent only, suggesting that the particles are not able to migrate into the pore system of this limestone. After drying, the mass increase was insignificant and the quantity of hydroxide estimated as potentially to be retained was not converted into dry matter, leaving less than 5% of the estimated amount.

4.2 Second set of experiments; application of the product to other materials

In order to understand the results obtained just after the first application, it was decided to test with other materials for comparative purposes. Taking into consideration the pore size distribution, one mortar and one limestone (identified as B) were selected to complement the study (see Figure 1b).

Limestone B is a very heterogeneous material, with some quartz and clay minerals in its composition. It has a high porosity (26-29%, at least). Absorption characteristics allow us to considerer that water percolation is much easier and the pore system can accommodate it in larger amounts. However, the characteristic considered as more relevant for this study is its pore size distribution, with the presence of a modal class between 500-1300nm, which in principle would be able to easily accommodate CaLoSil 50. In what concerns the selected mortar, it is a "weak" lime mortar removed from an outdoor test panel, having a low mechanical resistance (Costa 2010). The complete information about the water porosity of this material is still lacking and Hg porosity is probably insufficient to characterize it.

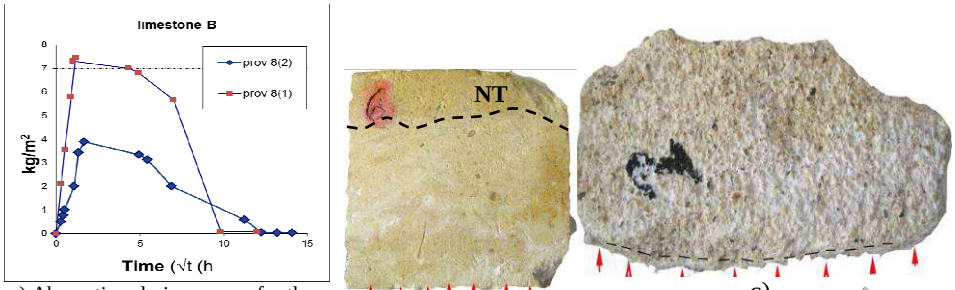
The consolidation product was applied in conditions similar to those previously described. However, the time of contact was adjusted, taking into consideration the characteristics of each material. Table 3 presents the absorption characteristics of these materials determined with a solution of CaLoSil E50. The samples after consolidation are presented in Figure 4.

		Absorption dynamics Product absorbed (kg/m^2) /application time	Product retained Estimated (g)	Product retained Measured (g)
Limestone B	1st	8.1 / (1h 30min.)	0.56	0.19
	2nd	3.4 / (2h 45min.)	0.25	0.10
Mortar (P1)	1st	5.6 / (3h)	0.71	0.03
	2nd	8.4 / (3h)	0.70	0.02

Table 3. Quantity of product consumed and retained after treatment

On limestone B, less dry matter was retained during the second application although the contact time was much longer. On the mortar, a different situation was observed; the amount of dry matter is much smaller taking into account the amount of product absorbed. However, the difference between estimated and measured values allows us to say that only a small part of CaLoSil was able to penetrate and this behavior is probably due to the formation of a layer near the bottom where a filtration effect took place.

Copyright transfered



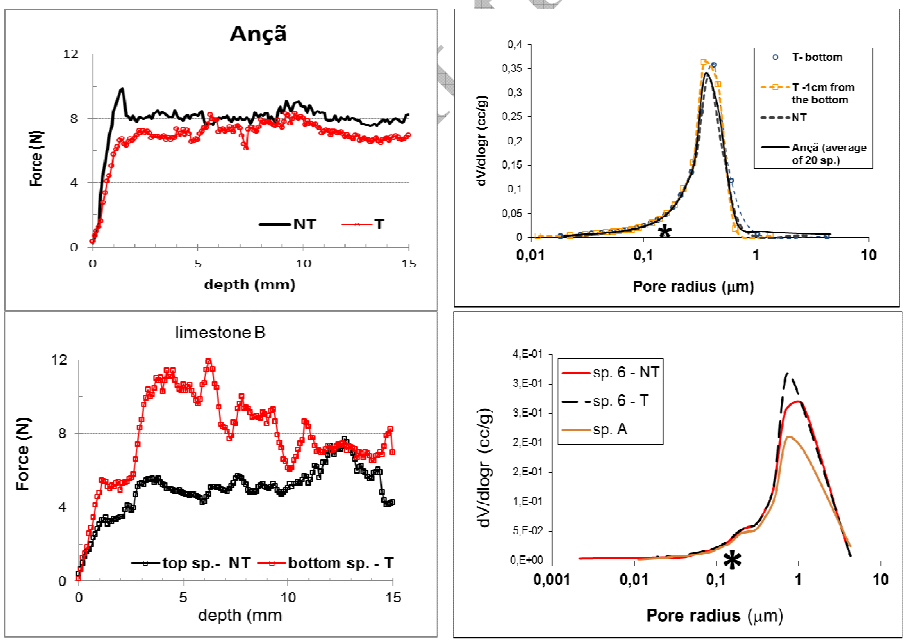
a) Absorption-drying curves for the . 1st (1) and 2nd applications (2)

Figure 4. Limestone B absorption curves (a). Limestone B and mortar after consolidation with CaLoSil E50 (b and c).

NOTE: The arrows indicate the face in contact with the product. In the case of limestone, the choice was to produce an interface T/NT as indicated in (a). On the mortar, the product was allowed to reach the top of the specimen. On both cases, only the first 2-5mm were in direct contact with the product and for this reason, the deposits clearly visible on the mortar (more irregular and less evident on the limestone) were formed during the migration of the product upwards.

4.3 Consolidation action

The consolidation effect was evaluated after 6 months in limestone A and after 3 in the case of mortar and limestone B. Drilling resistance is particularly useful to quantify the strength increase and it was performed using the conventional procedures described since the introduction of this technique (see Tiano 2000).



Registered

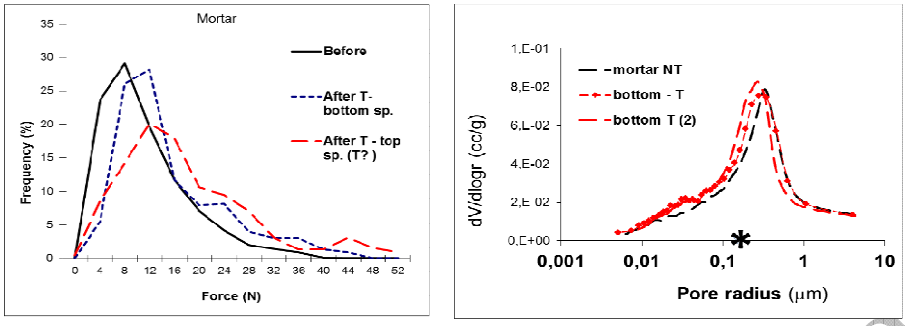


Figure 5. Consolidation effects on drilling resistance (on the left) and pore size distribution (on the right).

The method is particularly interesting when the material is homogeneous, and the interpretation becomes more difficult when it is heterogeneous or/and abrasive. Changes produced by consolidation on the original pore size distribution were also determined to evaluate this action. The results are presented in Figure 5 and Table 4.

	DR (N) [400rpm -10mm/min]		Hg porosity (<4µm) (%)	
	Before (NT)	After (T)	Before (NT)	After (T)
Ançã limestone	8.1 ± *0.4*	7.1 ± *0.5*	24.3	26.2-25.3
Limestone B	5.6 ± *3.2*	7.8 ± *3.6*	35.4	33.2
Mortar (P1)	8.6 ± *6.2*	13.1 ± *9.2* (top); 11.7 ± *7.3* (bottom)	15.5	17.1 - 16.9 (bottom) 15.2 - 16.5 (top)

Note: Mean values calculated between 1.0-11mm (Ançã and limestone B), and 0-11mm (mortar)

Table 4. Drilling resistance and Hg porosity before and after consolidation with CaLoSil E50

Drilling resistance is particularly informative in what concerns the evaluation of the effect in these materials; in Ançã stone (Fig. 5a) no evidence of consolidation could be found since the "non-treated" and "treated" zones show similar values. On the other hand, the consolidation effect is visible on limestone B and in the mortar. This limestone is very heterogeneous but drilling graphs show the difference between the two zones and the position of the interface (around 12 mm). On the mortar, the results obtained are widely scattered but the frequency distributions of the drilling resistance values indicate that the consolidant was able to increase resistance by about 3 to 5N. The results also indicate that the mortar was impregnated from the bottom to the top of the specimen.

In what concerns the changes on porosity, the results are not very clear and need further investigation. On Ançã limestone, all the three curves are very similar and overlap. On the mortar, the effect of the product on the range of pores under evaluation is also negligible, but the distribution only represents the smaller pores, since the macroporosity was not determined. Limestone B is in fact a very heterogeneous material and the results of Hg porosity also indicate this fact (see graphs of the non-treated specimens "sp A" and "sp. 6NT"); however, consolidation seems to have slightly decreased the total porosity apparently in the range of pores around 1µm.

The effect of consolidation on the water properties was also investigated. Water absorption by capillarity indicates that changes are negligible in both cases (Figure 5). However, in the face in contact with the product, water absorption values are visibly smaller after consolidation (Figure 5 right).

Copyright transfered

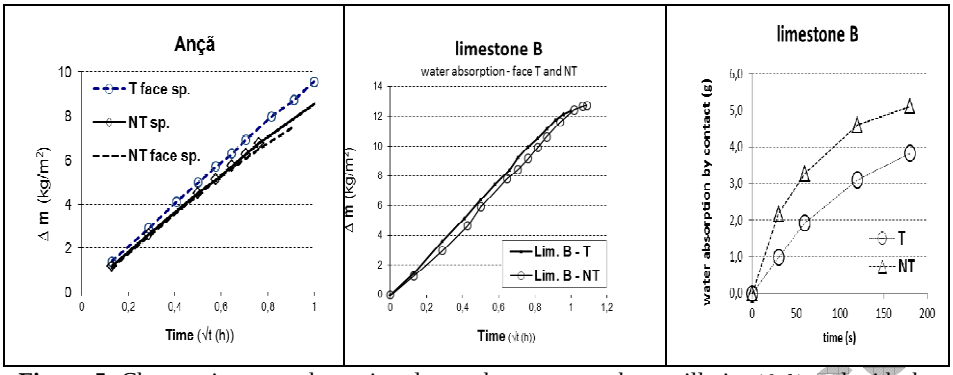


Figure 5. Changes in water absorption due to the treatment; by capillarity (left) and with the sponge method (right)

5. Conclusions

This paper presents the results of the first set of tests performed in the laboratory to evaluate the possibility of using CaLoSil E50 to consolidate a very porous limestone (Ançã). These first set of tests aimed to evaluate the impregnation capability and the resulting consolidation effect. Results have shown that the product is absorbed but it became clear that it was mostly the solvent that was able to migrate inside the pore system and a large quantity of nanoparticles ended up accumulated at the base of the specimen.

In order to clarify this behavior other materials were tested, namely one weak lime mortar and another very porous limestone. In both cases the results have shown an increase of hardness after treatment, as measured with a drilling technique. Changes promoted by the consolidation on the original water properties are less evident, fact that can be attributed to the low quantity of consolidant that was absorbed.

The experience demonstrated that this consolidation product does not have a significant penetration capability necessary to guarantee a mass consolidation effect. Moreover, the use of a very high concentrated product is not adequate for this purpose and may even have a harmful effect. Due to the accumulation of product at the surface, it can easily lead to the formation of a calcite surface layer, especially when the excess is not removed. The same phenomenon is expected to occur when the product is applied by brush and this behavior can be attributed to a selective migration of the components of the product (solvent and nanoparticles).

6. References

Bracci, S.; Sacchi, B.; Pinto, A.F. & Delgado Rodrigues, J. 2008. “Inorganic consolidants on stone artifacts: optimization of application procedures for marble and limestones”. International Symposium “Stone consolidation in cultural heritage: research and practice”, Lisbon 6-7 May, 2008. Proceedings, J. Delgado Rodrigues & João Manuel Mimoso (Eds.), pp. 81-90.

Campbell, A. ; Hamilton A. ; Stratford T. ; Modestou S. & Ioannou I. 2011. “Calcium hydroxide nanoparticles for limestone conservation: imbibition and adhesion”. Paper presented at the Symposium “Adhesives and consolidants for conservation: Research and applications, Ottawa, 17-21 October 2011. Proceedings available at http://www.cci-icc.gc.ca/symposium/2011/Paper%2029%20-%20Campbell%20et%20al.%20-%20English.pdf.

copyright transfered

Castro, E., Delgado Rodrigues, J. & Cravo, M.R.T. 1990 – *Estudos relativos à alteração e conservação da fachada da igreja de Santa Cruz, em Coimbra*, Lisbon, LNEC, Internal Report 176/90-NP/NQ (in Portuguese).
Costa, D.; Magalhães, A.; Veiga & R. 2010. "Characterization of mortars using DRMS. In situ and laboratory integrated testing". Paper presented at 2nd Historic Mortars Conference, Prague 22-24 September 2010. RILEM Bookseries, 2012, Volume 7, Part 4, 413-423.
Danehey, C., Wheeler, G. & Su, S.H. 1992. "The influence of quartz and calcite on the polymerization of methyltrimethoxysilane". Paper presented at the 7th Int. Cong. on Deterioration and Conservation of Stone, Lisbon, 15-18 June 1992. Proceedings, J. Delgado Rodrigues, F. Henriques & F. Telmo Jeremias (Eds.), volume 3, pp. 1043-1052.
Daniele V., Taglieri, G. & Quaresima, R. .2008. "The nanolimes in Cultural Heritage conservation: characterization and analysis of the carbonatation process". *J. Cult. Heritage.* 9: 294–301.
Daniele, V. & Taglieri G. 2010. "Nanolime suspensions applied on natural lithotypes: the influence of concentration and residual water content on carbonatation process and on treatment effectiveness". *J. Cult. Herit*age. 11: 102–106.
Delgado Rodrigues, J. 2001. "Consolidation of decayed stones. A delicate problem with few practical solutions". Paper presented at Historical Constructions 2001 conference, Guimarães. Proceedings, P.B. Lourenço & P. Roca (Eds.), pp. 3-14.
Delgado Rodrigues, J., Ferreira Pinto, A.P. & Belém, A. 1997 – *Estudo de tratamentos de conservação para a fachada da igreja de Santa Cruz* . Lisbon, LNEC Internal Report 100/97-GERO (in Portuguese).
Drdácky, M. & Slízková, Z. 2008. "Calcium hydroxide based consolidation of lime mortars and stones". Paper presented at the International Symposium "Stone consolidation in cultural heritage: research and practice, Lisbon 6-7 May, 2008. Proceedings, J. Delgado Rodrigues & João Manuel Mimoso (Eds.), pp. 299-308.
Ferreira Pinto, A.P. 2002. "Conservation of carbonate stones. Study and selection of treatments", (in Portuguese), PhD dissertation. Technical University of Lisbon, Instituto Superior Técnico.
Hansen E.; Doehne E.; Fidler J.; Larson J.; Martin B.; Matteini M.; Rodríguez-Navarro C.; Sebastian Pardo S. ; Price C. ; De Tagle A., Teutonico, J. M & Weiss, N. 2000. "A review of selected inorganic consolidants and protective treatments for porous calcareous materials". Available at http://publicationslist.org/data/eric.doehne/ref-59/2003_EH_EDoehne_Inorganic_Conso.pdf.
Pamplona, M; Kocher, M.; Snethlage, R. & Wendler, E.2008. "Consolidation effectiveness of TEOS on Ancã limestone from Portugal - a laboratory study". Paper presented at the International Symposium "Stone consolidation in cultural heritage: research and practice, Lisbon 6-7 May, 2008. Proceedings, J. Delgado Rodrigues & João Manuel Mimoso (Eds.), pp. 183-192.
Pinto, A.F. & Delgado Rodrigues, J.2008. "Hydroxylating conversion treatment and alkoxysilane coupling agent as pre-treatment for the consolidation of limestones with ethly silicate". Paper presented at the International Symposium "Stone consolidation in cultural heritage: research and practice, Lisbon 6-7 May, 2008. Proceedings, J. Delgado Rodrigues & João Manuel Mimoso (Eds.), pp. 131-110.
Tiano, P. ; Delgado Rodrigues, J. ; De Witte, E. ; Vergès-Belmin, V. ; Massey, S.; Snethlage, R. ; Costa, D. ; Cadot-Leroux, L. ; Garrod,E & Singer, B. 2000. "The conservation of monuments: a new method to evaluate consolidating treatments". *Int. J. Restoration Buildings Monuments*, 6 (2): 133–150.
Tiano, P.; Pardini,C. 2004. "Valutazione in situ dei trattamenti protettivi per il materiale lapideo. Proposta di una nuova semplice metodologia ". *Arkos*, 5: 30–36
Wheeler, G. ; Fleming, S. & Ebersole, S. 1992. "Comparative strengthening effect of several consolidants on Wallace sandstone and Indiana limestone". Paper presented at the 7th Int. Cong. on Deterioration and Conservation of Stone, Lisbon, 15-18 June 1992. Proceedings, J. Delgado Rodrigues, F. Henriques & F. Telmo Jeremias (Eds.), volume 3,: 1033-1038.

Copyright transfered