

Original article

Stone consolidation: The role of treatment procedures

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Received 18 April 2007; accepted 5 June 2007

Abstract

Four types of carbonate stones and three consolidation products were used in a systematic study to assess the influence of the application procedures on the amount of product applied, as a primary step to evaluate consolidation treatments. Microdrilling, ultrasonic velocity and flexural resistance were used as performance indicators. The amount of product of a specific treatment and its action depend on the application procedures, both when the treatments are carried out in the laboratory and on site. The results are expected to contribute to the standardisation of testing protocols on stone consolidation.

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Keywords: Consolidation treatment; Carbonate stones; Consolidation procedures; Penetration depth; Resistance increase; Microdrilling; Ultrasonic velocity; Flexural resistance

1. Research aim

The main objective of this research was the testing of methodologies for the study of consolidation treatments. A detailed analysis of the importance of treatment procedures on the amount of product absorbed, on the penetration depth and on the main mechanical properties of the consolidated layers was its main aim. Through an extensive series of parametric tests it also aimed at finding the best methodologies for the scientific justification and assessment of effectiveness, harmfulness and durability of treatments under natural and artificial conditions. A study of on-site case studies was performed as a complement to laboratory results and aimed at contributing to a better approximation of the real behaviour of stone consolidation actions. The on-site performance evaluation of some commercial products widely used for consolidation of carbonate stones was included.

2. Introduction

From the available references, very little is known about the dependence of the consolidation action on the procedures adopted in the application of the consolidating product. Frequently, published studies on consolidation compare the performance of products applied with different protocols, disregarding the fact that slight differences in the application protocols may bring about significant differences in the results. Relevant parameters include differences in the contact time when products are applied by capillarity, differences in the water content of the support or in the brushing strokes. These inconsistencies are responsible for the difficulty in integrating research knowledge and are a constraint on the improvement of the conservation practice.

Conservation of stone objects is always a delicate and complex problem. Multiple variables have to be taken into account to identify the problems, define the necessary conservation actions and to select materials and procedures to be used. The variety of factors to be analysed include the intrinsic stone properties, the state of conservation, the forms of degradation, the degradation mechanisms and the environment factors. It is then necessary to select the appropriate materials and procedures for a correct conservation treatment.

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Consolidation is used to improve the cohesion of weathered stone when serious decay patterns and in-depth cohesion loss are present. Consolidation treatments are the most risky conservation actions due to their irreversibility and the likeliness to cause undesired effects, such as the possible loss of the surface that was supposed to be preserved. This risk justifies the numerous studies that have been developed on stone consolidants.

In general, inorganic products, such as calcium hydroxide, barium hydroxide and ammonium oxalate, are mainly addressed to act in the very superficial layers due to their low penetration capacity [1–3]. Yet, some specific uses in surface consolidation or passivation have been pointed out as important potential uses of inorganic consolidating products. Other consolidants, namely alkoxysilanes, acrylic and epoxy resins, have been widely used in stone conservation and multiple references on them can be found in the specialised bibliography [4,5].

Alkoxysilane-based formulations have undoubtedly been the most widely used materials for the consolidation of stone outdoors, mainly due to their ability to penetrate easily into porous materials. They are also favourably compared to other organic-based products, for the lesser impact on the permeability and drying properties of the consolidated stones. Two compounds, in particular, have been dominant: methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS), in general used under the form of oligomers. These consolidants are absorbed by the stone, hydrolyzed by water to form silanols that then polymerise in a condensation reaction and form a polymer that produces the required strength increase.

The poor chemical affinity between calcite and the silica molecules formed after hydrolysis and condensation of alkoxysilanes [6] and the tendency to crack during shrinkage and drying due to the gel brittleness have been responsible for several studies with the objective of modifying and improving alkoxysilane performance [7,8]. With these known drawbacks, the use of alkoxysilane-based products for the consolidation of carbonated stones results from the lack of more adequate alternatives.

Acrylic-based resins have been also frequently used in stone conservation, namely the acrylic resins dissolved in organic solvents, such as Paraloid B72 (Acryloid B72). They can promote a substantial increase of stone strength, although they are able to impregnate a thin outer thickness of stone only.

The epoxy resins can promote a greater increase in mechanical strength than silanes or acrylic consolidants. Concerns about this kind of product include the lack of reversibility, excessive colour changes, and viscosity, but the real problem appears to be that suitable methods of application are not well established.

Selwitz [9] has reviewed the use of epoxies as consolidants, indicating successes and failures. He highlights the pioneering work of Domasłowski and Gauri, in particular, and emphasises the two different paths they have adopted in order to treat relatively small objects and large façades, respectively. The choice of the solvent, the application procedures and post-

application care are vitally important to reach a successful treatment. Domasłowski in 1969 tested applications with a “pocket system” that was intended to hold the consolidant against the stone, while Mirowski in 1988 described a system of bottles for maintaining a steady supply of the consolidant at a large number of contact points. Schoonbrood developed in 1993 a low-pressure application technique that maximises capillary absorption and Hempel has applied a vacuum system to facilitate the penetration into movable objects.

Cavaletti et al. [10] introduced cyclo-aliphatic epoxy resins and applied such a resin to consolidate large columns of decayed granite, by using a vacuum-assisted impregnation technique.

In conservation practice, consolidants are usually applied to the surface of the stone by brush, although applications by spraying or by long-lasting direct contact might be interesting alternatives. In the laboratory, researchers have adopted a wide variety of application protocols to carry out consolidation. For instance, Tabasso and Santamaria [11] used capillarity absorption for 20 h, while De Witte et al. [12] applied capillarity for only 15 min. Bradley [13] applied drops with a pipette until saturation, Valdeón et al. [14] used capillarity until total saturation, Kumar and Ginell [15] used spraying and capillary rise, Maravelaki et al. [16] applied consolidant by capillary absorption, brushing and with a pipette, and Delgado Rodrigues and Costa [17] used capillarity for 24 h or a 2-step immersion for 24 h. However, to our best knowledge, no specific and systematic study of the influence of the application protocols on the performance of stone consolidants has been carried out so far. In general, the studies did not pay particular attention to the importance that the application protocols may have on the performance of the consolidation treatments, although some researchers have warned of the influence of the application conditions on the consolidation action as well as of its dependence of the stone characteristics [18].

The performance of a consolidation treatment depends not only on the product and on the stone characteristics, but also on the procedures used for the application of consolidants and possibly on the stone and ambient conditions existing before, during and after the product application. This complexity is encompassed under the term “treatment”, a notion that needs to be further detailed.

The concept of “treatment” is not currently adopted when stone conservation is involved. The majority of the research studies in this field have been concerned with the study of specific aspects mainly related to the chemical behaviour of consolidants and less with the potential performance of the products when applied in real situations. For instance, stone powders have been used to study chemical reactions, but usually the results are not validated directly on stone surfaces. In other studies, the products are tested on stones but their action is not directly evaluated with the objective of identifying and quantifying the main characteristics that desirably should be altered by the treatment.

Sasse [19] based on previous studies of his team [20,21] has shown that the performance evaluation needs to integrate multiple variables, and in this same vein Delgado Rodrigues and

Grossi [22] have proposed a general approach to assess the compatibility of consolidants.

Consolidation depends on the type of product, the chemical nature of solvents and the concentration of solutions. In our approach, a consolidation “treatment” is the result of applying a given product following a specific protocol and it shall be defined by taking into account all relevant aspects, such as:

- stone type and properties: major chemical constituents, physical characteristics (porosity, pore size dimensions, water absorption), mechanical characteristics (drilling resistance, ultrasonic velocity, surface hardness), dimension of the surface under treatment;
- characteristics of the product: chemical nature of the consolidant and solvents, concentration taken as reference;
- application procedure: application process, number of applications, time interval between applications;
- amount of product to be applied or to be retained by the stone;
- ambient conditions required during and after treatment and the indication of limiting conditions (temperature and RH ranges, for instance);
- stone conditioning (water content, surface condition, etc.).

This paper addresses the consolidation achieved with several consolidation treatments and demonstrates its dependence on the stone lithotype, the type of product, the procedure adopted for the application of the product and the amount of product absorbed. The research was developed on four carbonate stones and with three consolidating products (ethyl silicate, acrylic and epoxy resins) and is supported in laboratory and in on-site tests. The consolidation achieved by the treatments was evaluated through microdrilling, ultrasonic velocity and flexural resistance. The results demonstrate that consolidation can only be defined in strict relation with the treatment that produces it, and show that its study shall be carried out under conditions directly resulting from the application of a defined amount of the specific product following a pre-defined application procedure.

3. Materials and methods

3.1. Stone materials

The laboratory experiments were carried out on four carbonate stones of different intrinsic properties that correspond to varieties present in many historic buildings in Portugal. Ançã and Boiça stones are very pure calcitic limestones almost exclusively formed of calcite. Both are quarried in the Coimbra region. Ançã stone is a very homogenous and fine grained white stone, having very high porosity. Coimbra and Lisbon stones are yellowish, mainly constituted of dolomite, which are quarried from Coimbra and Lisbon regions, respectively. Coimbra stone is a heterogeneous material and may show iron spots. Tables 1 and 2 present some properties of the selected stones.

The petrographic study of thin sections of Ançã stone shows that it is a calcitic vase with minor organic remains irregularly spread in the matrix and brown dendritic structures (probably iron oxides). Boiça stone is a homogeneous micritic matrix with frequent fossil remnants and veinlets of crystallised calcite.

Thin sections of Coimbra stone reveal zones with distinct characteristics. In some areas the stone is homogeneous and fine-grained, with no impurities, while other areas show a pervasive network of dendritic features filled or delineated with a brownish substance. Ferruginous intraclasts with round regular forms are also observed. Coimbra stone is brecciated in some cases with an important presence of fissures filled with iron oxides or calcite.

Lisbon stone is a fine-grained micrite having frequent vacuoles with diverse forms and dimensions. Some of these vacuoles are visible to the naked eye. The borders of the vacuoles are made of well developed dolomite crystals and frequently with perfect rhombohedral forms.

Ançã stone is a very pure limestone with 96% calcium carbonate (estimated from the CaO content of Table 2) with silica as the main accessory mineral. Boiça stone is mainly calcium carbonate (92%) and registers the presence of silica and some other accessory minerals.

According to the classification of Cayeux [23] (quoted in Carozzi [24]), Coimbra and Lisbon stones are calcitic dolomites, with 84% and 76% of dolomite, respectively (estimated from the MgO content of Table 2). The presence of silica and alumina in both stones points out the possible presence of clay minerals.

The Ançã and Boiça stones have quite different porosities, but both present a typically unimodal pore size distribution characterised by the presence of larger pores (0.05 to 1 µm) in Ançã than in Boiça stone (0.01 to 0.2 µm), Fig. 1. The heterogeneity of Coimbra stone is so pronounced that in some areas it is possible to visually identify zones where the stone is softer and more porous (Z1) than in others that are characterised by their lower porosity and higher hardness (Z2). The pore size distribution of Coimbra stone from the more porous material (Z1) and Lisbon stone present a tendency to be bimodal with the presence of graduated and extensive pore sizes, Fig. 1. This tendency for the polymodal distribution can be related to the process of dolomitisation [25]. The pore size distribution of Coimbra stone representative of the material with lower porosity (Z2) indicates that the pore space is made of pores with larger dimensions than those present in the more porous zones (Z1).

Although the methods available to evaluate treatments on site are scarce, the performance of the treatments under real conditions is fundamental for the correct understanding of their applicability. Sasse and Sneath [21] stress this importance and propose that the treatment performance should be evaluated under real situations, whenever the laboratory studies had pointed out the products to be promising.

To complement the laboratory studies, some areas from Portuguese monuments were selected to study some consolidation treatments under real conditions. Three monuments

Table 1
Some basic properties of the selected stones

Stone	Real density (kg m ⁻³)	Open porosity (%)	Water absorption under low pressure (pipe method) (RILEM II-4) (cm ³) (at 1 h)	Flexural strength (MPa)	Ultrasonic velocity (m s ⁻¹)
Ançã	2711 (±3)	27.2 (±1.1)	4.000 (in less than 6 min)	5.2 (±0.4)	3200 (±100)
Boiça	2710 (±5)	9.6 (±1.1)	0.500 (±0.100)	14.0 (±1.4)	4750 (±200)
Coimbra	2853 (±44)	17.8 (±3.3)	0.775 (±0.275)	11.6 (±2.1)	4520 (±260)
Lisbon	2846 (±17)	15.4 (±1.7)	0.475 (±0.150)	16.0 (±1.2)	4950 (±120)

located in Coimbra and one in Lisbon were selected. Celas Monastery is located in Coimbra and was selected for testing consolidation treatments on Ançã stone. Sub-Ripas Palace and the University of Coimbra were selected to test some stone elements similar to the Coimbra stone used in laboratory studies. S. Julião fortress is located in the surrounding of Lisbon city and the tested areas are similar to the Lisbon stone tested in laboratory experiments.

Specific areas in these buildings were selected and characterised, and samples were collected for evaluation of physical properties, such as porosity, water absorption, and real density. The on-site water absorption was measured with the pipe method according to the RILEM II.4 [26] standard.

The physical properties of the collected samples, complemented with information taken from other studies [27, 28] point out that:

- The stone elements of Celas Monastery are made of limestone similar to the Ançã stone used in the laboratory studies although slightly stronger (Fig. 2), with slightly lower porosity (23–26%) and absorption capacity (4 cm³ of water absorbed in 30 min with the pipe method).
- The characterisation of samples from Sub-Ripas Palace stone elements and the on-site tests performed confirm that the tested areas are made of stones similar to the Coimbra stone. The samples tested had 14–19% porosity, 2850–2890 kg m⁻³ real density and a heterogeneous strength, as displayed in Fig. 3.
- X-Ray diffraction of samples from the University of Coimbra identified dolomite as the most frequent mineral, with calcite and a minor amount of montmorillonite. The stone in the University of Coimbra is heterogeneous and contains significant fissuring that is responsible for the

- variable water absorption obtained with the pipe method (0–3.2 cm³ after 1 h). This indicates that the stone present in University of Coimbra is similar to the Coimbra stone.
- The samples from S. Julião Fortress have porosity (12%) similar to the Lisbon stone. However, they have lower real density (2450 kg m⁻³) and distinct capacity of water absorption (0.1–1.2 cm³ after 60 min.) when compared to the properties of Lisbon stone of the laboratory studies.

Table 2
Stone chemical results of the selected stones

(%)	Ançã	Boiça	Coimbra	Lisbon
(MgO)	0.61	1.78	18.4	16.67
(CaO)	53.55	51.44	26.8	31.13
(SiO ₂)	2.8	2.5	7.0	5.15
(Al ₂ O ₃)	0.23	0.53	1.4	1.35
(Na ₂ O)	0.03	0.04	0.35	0.05
(K ₂ O)	0.12	0.31	0.65	0.84
(Fe ₂ O ₃)	0.11	0.52	1.7	1.53
H ₂ O	0.08	0.14	0.35	0.22
Loss on ignition	42.5	42.1	42.0	42.6

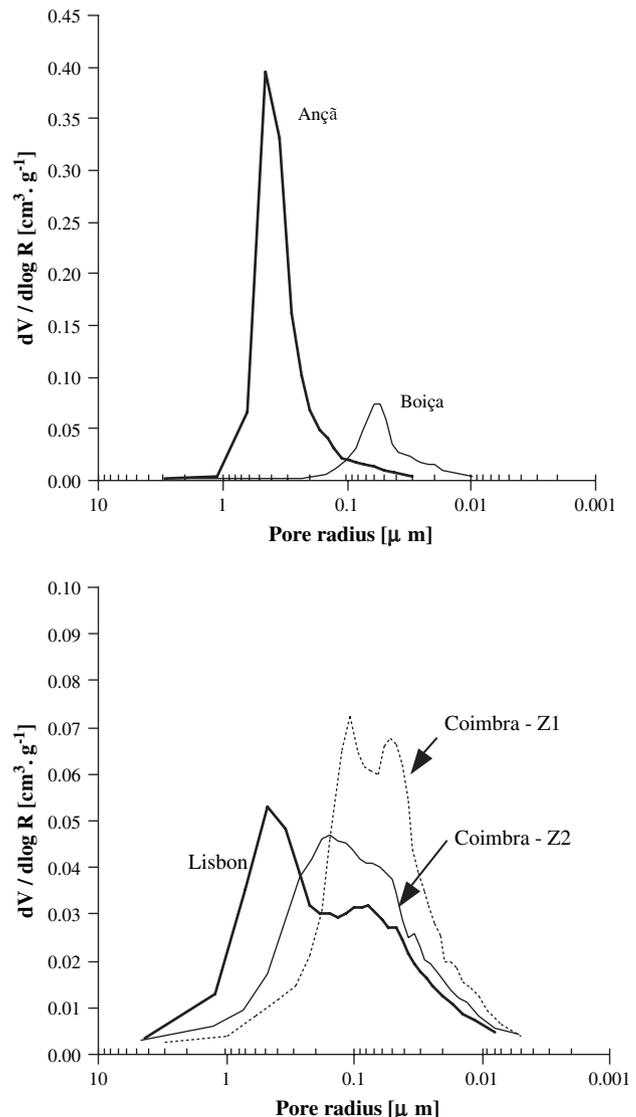


Fig. 1. Pore size distributions of the selected stones.

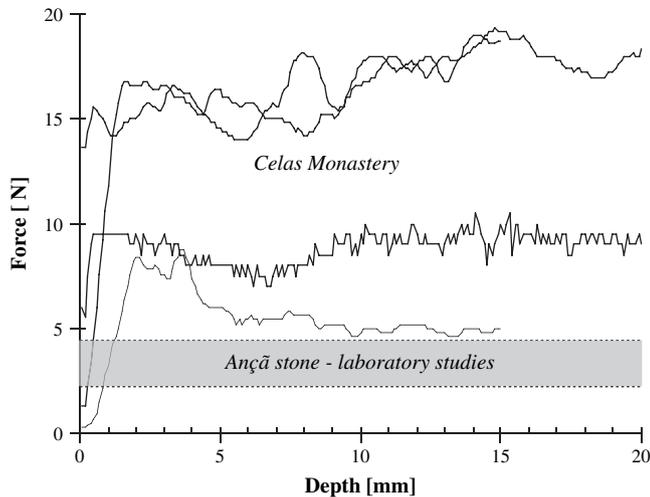


Fig. 2. Drilling resistance measured on stone elements of Celas Monastery compared with the drilling resistance characteristics of Ançã stone studied under laboratory conditions (shaded area of the graph).

3.2. Treatment products

Three commercially available consolidants were applied to each lithotype. Designation, manufacturer, solution applied, acronym, specific gravity and Brookfield viscosity are shown in Table 3.

The ethyl silicate (TG) contains a pre-polymerised TEOS mixed with white spirit as described by De Witte and collaborators [12]. The technical sheet indicates that the minimum deposition of gel of silica is 34% and the density at 25 °C is 0.95 g cm⁻³. This product is used as received.

The acrylic consolidant Paraloid B72, produced by Röhm and Hass, is described by the manufacturer as an ethyl-methacrylate copolymer, but is identified in the literature as an ethyl-methacrylate/methyl-acrylate copolymer (PEMA-PMA) [11,29]. It has a vast history of applications in the conservation field. The necessity to study solutions with low concentration

led to the use of the acrylic resin in the solid form, for subsequent preparation of the impregnation solution. According to the manufacturer, the solid product has a density at 25 °C of 1.15 g cm⁻³, a parameter of solubility of 9.3, being compatible with several solvents, namely toluene, xylene and acetone. Paraloid B72 was applied with the following formulation: 0.06:0.61:0.09:0.2 = resin/toluene/xylene/acetone and will be referenced in this paper with the acronym B.

The epoxy consolidant is a system of two components (a resin and a hardener) that has been applied in the preservation of a number of important stone monuments in Italy. The resin is a cycloaliphatic epoxy resin, EP 2101, produced by EUROSTAC, in the form of a 25% solution in toluene and isopropanol [10]. The hardener is an aliphatic polyamine solution that is mixed with the resin to provide a consolidating system in a proportion (hardener/resin) of 1:5 in weight. From the technical sheet, the resulting properties are: dry residue of 25%, viscosity (25 °C) of 10 mPa s and density (20 °C) of 0.85 ± 0.05 g cm⁻³. The induction and application time is dependent on the temperature when the components are blended. According to the manufacturer, the product can be diluted by using a mixture of toluene and xylene in a proportion of 1:1 to reduce its consolidating effect. In the present study, that method was used to dilute the consolidant in the proportion consolidant/solvent = 1:1 by weight. This product will be referenced in this paper with the acronym EP.

According to the manufacturer, TG should be applied until the saturation of the support, being understood that this point is achieved when the surface remains wet for 1 min. EP consolidant should be applied until saturation, taking care that the surface must remain wet in order to guarantee the continuous absorption of the product. The technical sheet of the acrylic product does not recommended specific procedures that should be respected in its application.

3.3. Application procedures

Consolidants were applied on the dry stone materials stabilised under laboratory conditions for at least 1 month. Specimens with different sizes and forms were treated by capillarity, by immersion and by brushing to evaluate the influence of the application procedure on the absorption of products and on the subsequent consolidation.

The treatments by capillary absorption were performed on 5 × 5 × 10 cm prismatic specimens, one for each lithotype with the exception of Coimbra stone, for which two specimens were tested. One face of 5 × 5 cm was placed in contact with the consolidant for 3 h, taking adequate measures to minimise the solvent evaporation during the application period.

The treatments by immersion were performed on prismatic specimens of 2.5 × 2.5 × 10 cm, 2.5 × 2.5 × 5 cm, 3 × 3 × 12 cm and 3 × 3 × 6 cm, on at least 11 specimens for each pair stone/consolidant. Immersion lasted 3 h or 24 h (14 h for EP) to achieve maximum penetration, a good approximation as to what could be expected from a fully impregnated specimen, and to evaluate the importance of the immersion time on the consolidation action. Five specimens were treated

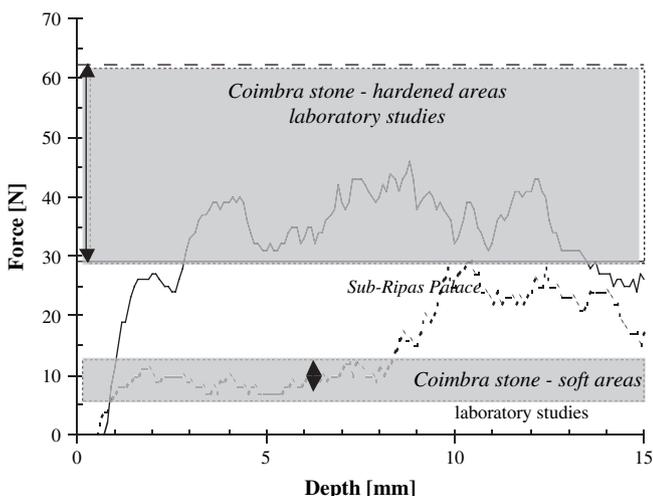


Fig. 3. Drilling resistance and heterogeneity identified on two stone elements of Sub-Ripas Palace and its comparison with Coimbra stone studied under laboratory conditions (shaded areas of the graph).

Table 3
Properties of the used consolidation products

Designation	Manufacturer	Solution applied	Acronym	Specific gravity (g ml ⁻¹)	Brookfield viscosity (mPa s)
Tegovakon V	Goldschmidt	Ready to use	TG	0.95	15
Paraloid B72	Röhm and Hass	Dissolved at 0.06:0.61:0.09:0.2 (resin/toluene/xylene/acetone)	B	0.84	11
EP 2101	EUROSTAC	Diluted in 1:1 in a mixture of toluene/xylene (1:1), in weight	EP	0.88	8

during 24 h (14 h for the epoxy consolidant) and at least one for the 3 h immersion. The longest time of immersion performed with the EP product was 14 h, since this period corresponds to the longest span of applicability after its preparation, for the temperature range prevailing when it was prepared and applied.

Stone slabs with about 3 cm thickness and 100–300 cm² surface and cubic specimens of 5 × 5 × 5 cm were consolidated by brushing until apparent refusal in order to achieve a treatment similar to those usually carried out in real situations. The apparent refusal was considered to be reached when the surface remained wet for 1 min. The treatment was carried out by brushing at least four stone slabs and four cubic specimens per consolidation treatment. For each product the application by brushing was done as follows:

- TG (ethyl silicate): two applications in the same day with a time interval of 4 h between them and the repetition of this procedure 2 days later;
- B (acrylic resin): two applications in the same day with a time interval of 4 h;
- EP (epoxy resin): one application.

To guarantee the necessary correspondence between the laboratory studies and field practice, some treatments were performed on site by brushing with the same products tested in the laboratory. The products were applied until saturation of the support was reached, this being understood to occur when the surface remained wet for 1 min, as performed in the laboratory treatments.

On site, other time intervals between applications were used besides the ones that were carried out under laboratory conditions.

Immediately after the application, the surfaces were gently cleaned with pure solvent in a soft cotton tissue to avoid the accumulation of product on the surface and the formation of superficial deposits or thick films. At least 1 month elapsed between the application of the products and the evaluation of the corresponding consolidation action.

3.4. Testing methods

For the quantification of the amount of product involved in the treatment for each situation under analysis, the following parameters were determined: the amount of product absorbed, the dry mass residue and the amount of product consumed (in the case of brush applications). The quantification on site was made through the evaluation of the amount of product consumed per unit surface under treatment.

The amount of product consumed by brushing was defined as the amount of product applied in weight of product per unit surface (kg m⁻²) under treatment. The amount of product consumed was obtained through the mass difference of the recipient with the product before and after treatment. This quantification is very useful, because it is the only way to provide information for the conservation practice in terms of the specification of the amount of product [30].

The amount of product absorbed by brushing, capillarity and immersion application was determined by weighing the specimens before and immediately after treatment and is expressed as the weight of product per unit surface (kg m⁻²) in contact with the products.

The consolidation effect was quantified by microdrilling resistance, ultrasonic velocity and flexural strength.

The drilling resistance measurement system (DRMS) has been developed as an attempt to design a portable system capable of carrying out minimally destructive tests in the laboratory and on site based in microdrilling. Further information about the technical and scientific background can be found in Tiano et al. [31,32]. The DRMS makes it possible to obtain the drilling resistance based on the measurement of the force necessary to drill a hole under specific operating conditions. Recent results obtained with the DRMS place this methodology as the most promising for the evaluation of the consolidation performance, particularly in relatively soft stones [31–36]. In this study current tungsten drill bits with 5 mm diameter were used with a rotation speed of 400 rpm and penetration rate of 15 mm min⁻¹.

Table 4
Products application by brush: amount of product consumed and absorbed

Stone	Amount of product consumed (kg m ⁻²)			Amount of product absorbed (kg m ⁻²)		
	TG	B	EP	TG	B	EP
Ançã	3.3 (±0.65)	4.9 (±1.60)	6.0 (±1.12)	2.3 (±0.54)	2.1 (±0.68)	4.0 (±1.50)
Coimbra	0.9 (±0.52)	1.7 (±1.71)	1.2 (±0.68)	0.4 (±0.06)	0.2 (±0.03)	0.4 (±0.09)
Lisbon	0.8 (±0.46)	1.2 (±0.70)	0.6 (±0.36)	0.2 (±0.05)	0.2 (±0.04)	0.2 (±0.03)
Boiça	0.6 (±0.40)	1.0 (±0.80)	0.7 (±0.41)	0.2 (±0.02)	0.1 (±0.03)	0.1 (±0.02)

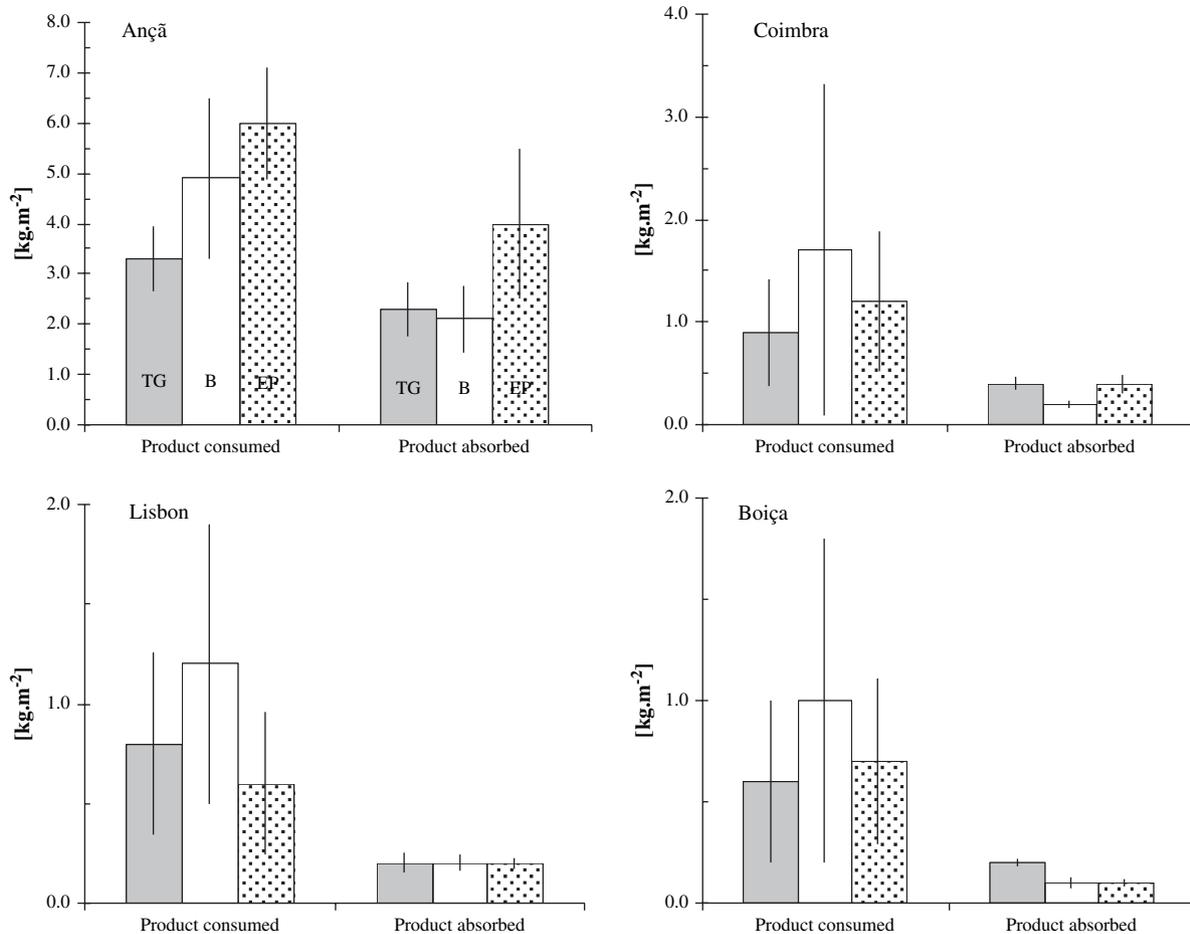


Fig. 4. Products application by brush on stone slabs. Total amount of product consumed and absorbed (sequence of bars is, from left to right, TG, B, EP).

The ultrasonic velocity is one of the non-destructive tests more widely used for evaluating mechanical characteristics of stone. 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. Ultrasonic measurements were performed in the laboratory on dry samples. The frequency used for the longitudinal velocity measurements was 45 kHz, in transmission mode, by using a pulse generator G. Steinkamp (BP-7) and cylindrical and tapered transducers both with equal vibration frequencies.

The increase in mechanical strength promoted by the consolidants was evaluated on the specimens fully impregnated by immersion. Strength was quantified by means of the flexural strength under concentrated load in a Lloyd Universal Testing Machine with a load cell of 10 kN. This test was carried out before and after consolidation.

4. Results and discussion

4.1. Absorption of products

Table 4 and Fig. 4 present the average values and the standard deviation of the amount of product for all the stone consolidation trials applied by brushing. The differences

between the amount of product absorbed and consumed are influenced by the degree of volatility of the solvents and the absorption capacity of the stone. In the situations under analysis, the amount of product absorbed was about 20%, 35% and 40% of the amount of product consumed, respectively for the products B, EP and TG. The higher difference was obtained for the application of product B, given the high volatility of acetone that represents 42.5% of the total mass of solvents present in the solution used.

The amount of product absorbed and consumed depends not only on the physical and chemical properties of the product but also on the pore space of the stone under treatment. Fig. 5 illustrates the dependence of the amount of product absorbed on the stone porosity. It is worth mentioning the weak absorption capacity revealed by stones with porosity lower than 18% and the apparent proportional increasing of this tendency for stones with higher porosity. As can be noticed in Figs. 4 and 5, the amount of consolidant absorbed is always much lower than the amount of product consumed, as a consequence of the volatility of the solvents, as mentioned before.

The amount of product absorbed under specific conditions defined to obtain a consolidation treatment depends also on the dimension of the surface under treatment, particularly

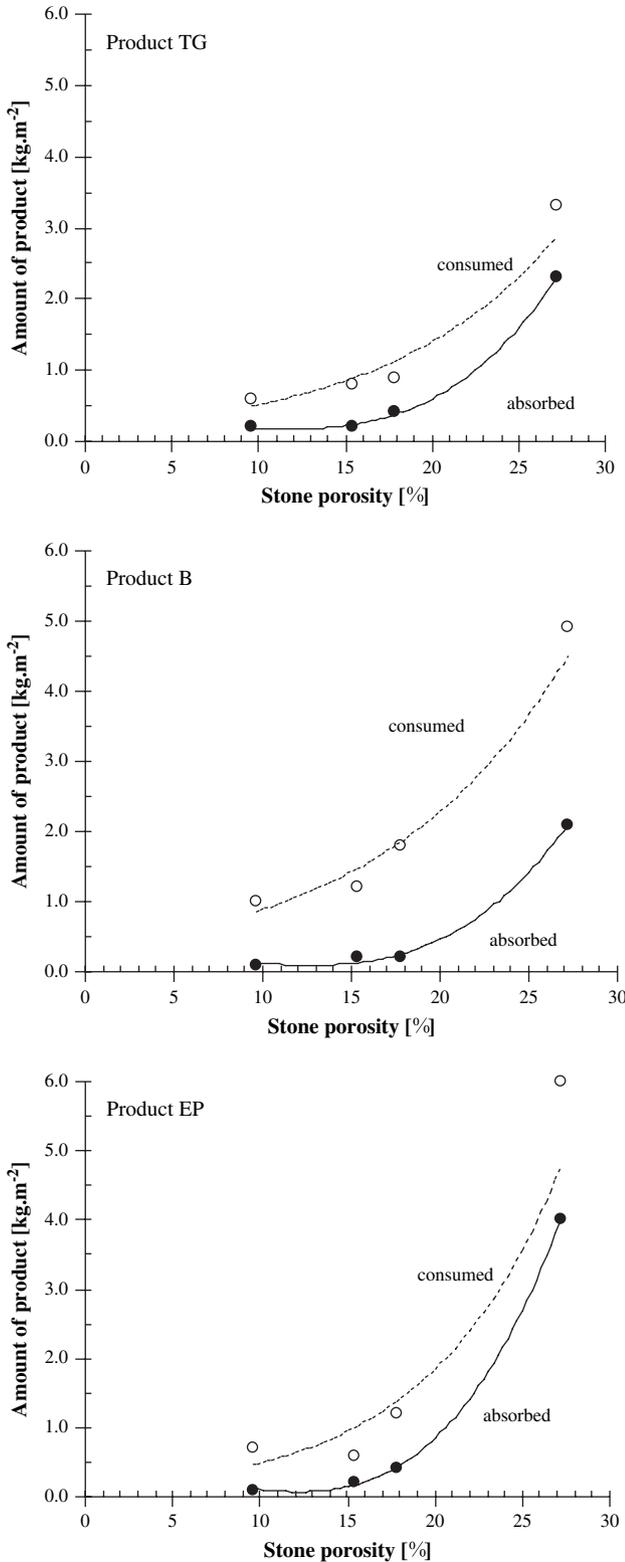


Fig. 5. Products application by brush. Average values of the total amount of product consumed and absorbed in function of stone porosity.

for the more porous stones and for products that have higher capability to penetrate inside the stone. Fig. 6 shows that on Ançã stone, the more porous one, it was possible to apply higher amounts of all the consolidants, under the same

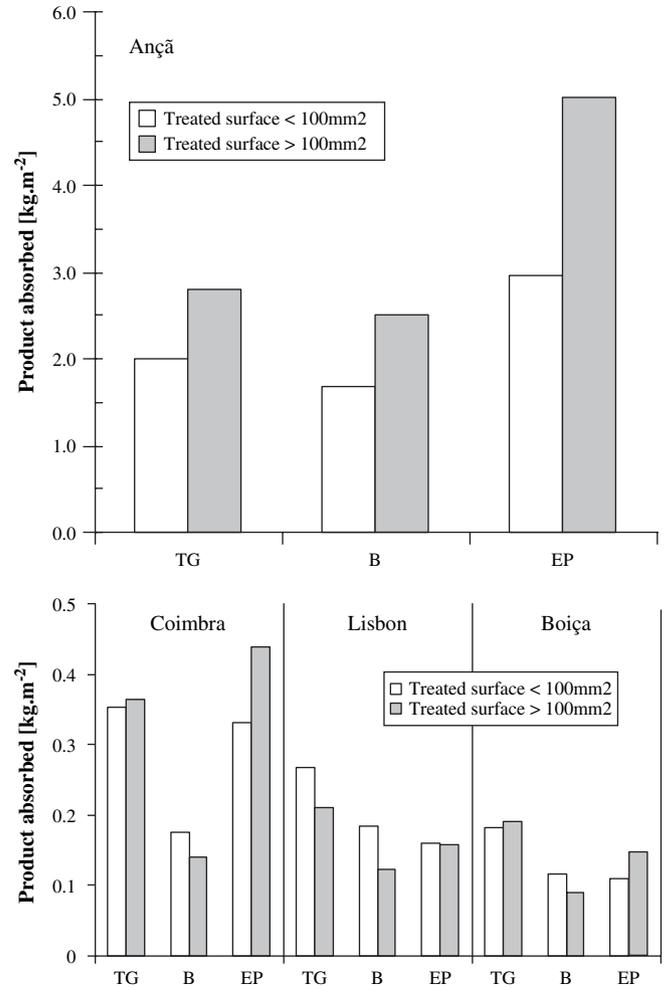


Fig. 6. Products application by brush. Influence of the dimension of the surface under treatment on the amount of product absorbed (average values).

treatment protocol, on the specimens with higher tested surfaces. For less porous stones this aspect seems to be not so relevant, as can be observed in Fig. 6.

The application of products by capillarity was carried out for a period of 3 h. This period was chosen because in most situations after 1 h 30 min the product migration fringe almost stopped, Fig. 7, with exception of Ançã stone when treated with products TG and EP. In Fig. 7 it is possible to observe the difficulty revealed by product B to get inside the stones, namely on Coimbra, Lisbon and Boiça stones.

Although the limited number of specimens obliges to take the results with care, it was possible to conclude that the treatments carried out by capillarity were responsible for higher amounts of product absorbed, Table 5, when compared to the ones obtained by brushing application (Table 4).

With the exception of Ançã stone, which absorbed appreciable amounts of consolidants by capillarity, all the other lithotypes absorbed small quantities, in general $\leq 1 \text{ kg m}^{-2}$. As in the treatment by brushing, the epoxy consolidant (EP) was the one that promoted higher amounts of product absorbed in all the stone varieties, with the exception of Lisbon stone in which the higher absorption was obtained with ethyl silicate (TG).

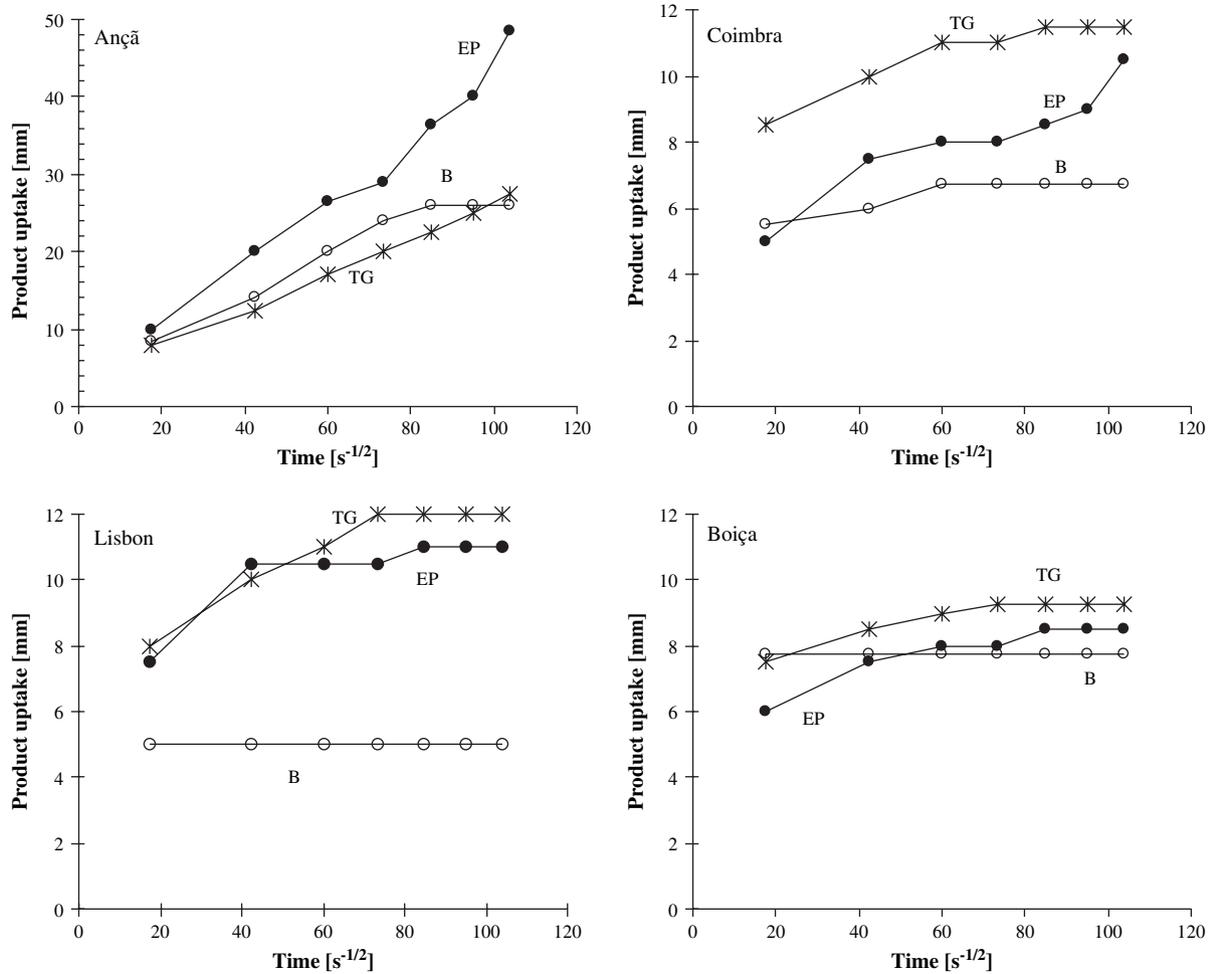


Fig. 7. Products application by capillarity. Evolution in time of the uptake fringe during treatment.

It is expected that the amount of consolidant absorbed by the stone influences the performance of the treatment. However, the technical sheets of the consolidants do not specify the amounts to be recommended and specific studies with the objective of establishing criteria or guidelines for obtaining adequate consolidation treatments, namely in terms of the amount of product that should be absorbed to achieve a desired consolidation action, have not been made, to our knowledge.

The amount of product absorbed has a clear influence within the same stone, as regards the penetration depth and the resistance increase of the treated stone layer. This influence can be observed in Fig. 8 in terms of the drilling resistance of the Ançã stone where specimens untreated and treated by brushing with different amounts of products are compared.

Table 5
Products application by capillarity (3 h): amount of product absorbed

Stone	Amount of product absorbed (kg m ⁻²)		
	TG	B	EP
Ançã	5.6	6.5	8.1
Coimbra	1.1	0.8	1.2
Lisbon	0.7	0.5	0.6
Boiça	0.4	0.4	0.6

The influence of the amount of consolidant on the consolidation action can also be analysed in terms of the drilling energy [35] as shown in the graph in the lower right in Fig. 8. This graph plots the drilling energy, computed as the integral of the drilling force for a drilling length of 20 mm. The graph clearly shows that the drilling energy is linearly proportional to the amount of product absorbed, for all products in the range of the studied amounts. Ethylsilicate induced the lowest increase, confirming the known poor consolidating capacity of ethyl silicates in carbonate stones. However, the drilling force (graph in the upper left) points out that an important increase of penetration depth can be achieved with it when the amount of consolidant is increased. The consolidation action promoted by the acrylic resin (B) seems to be more sensitive to the amount of product.

The behaviour identified in the laboratory was confirmed in onsite conditions as shown in Fig. 9, which compares the consolidation by ethyl silicate treatments carried out by brushing with two different amounts of product onto a column of Ançã stone from Celas Monastery. The treatments were performed with two similar ethylsilicates, Tegovakon V and Wacker OH. Both consolidants have densities around 1.0 g cm⁻³ and a content of ethylsilicate higher than 40%, according to the

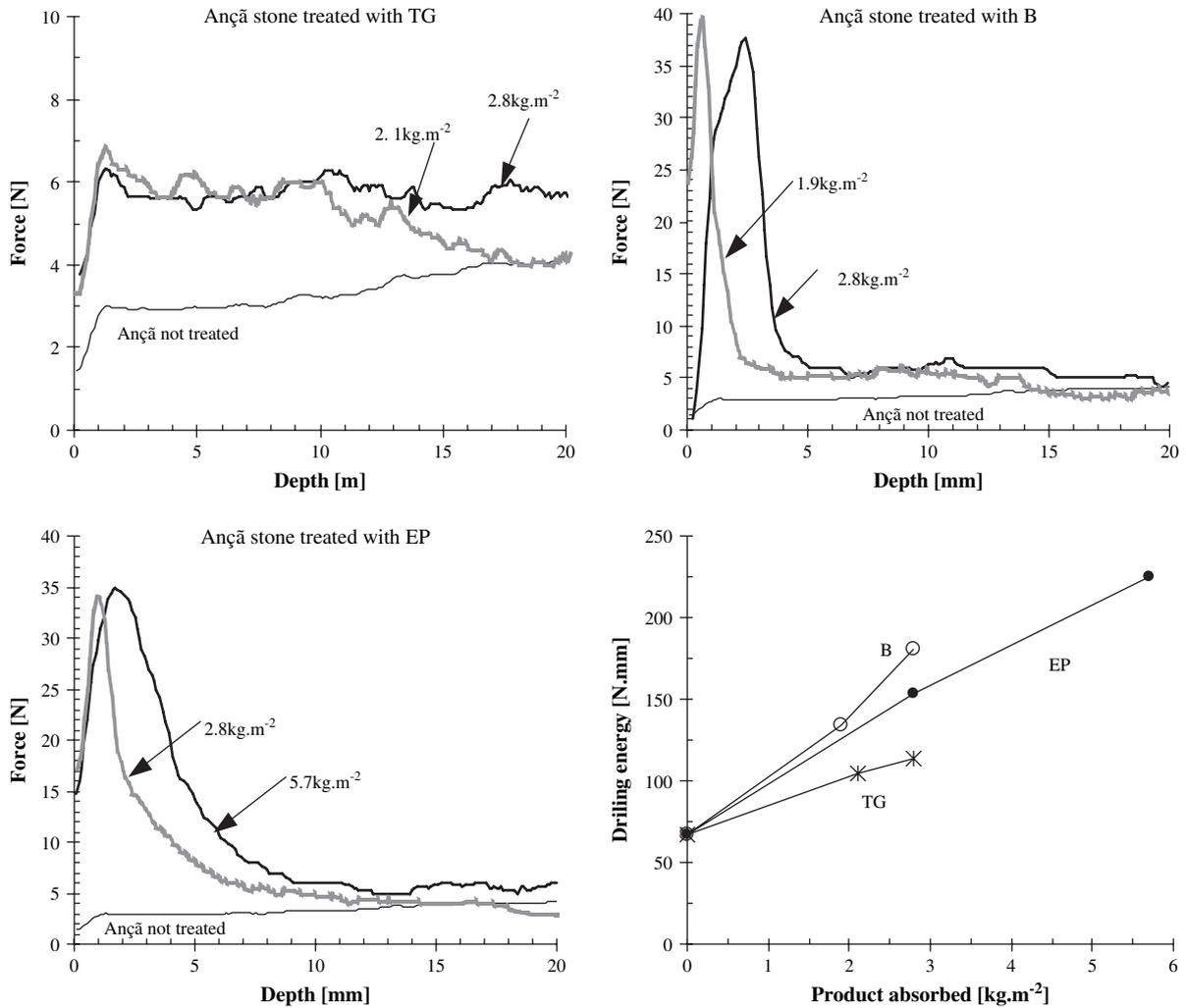


Fig. 8. Drilling resistance of Ançã stone for different amounts of consolidation products. The graph on the lower right represents the drilling energy computed for a hole depth of 20 mm.

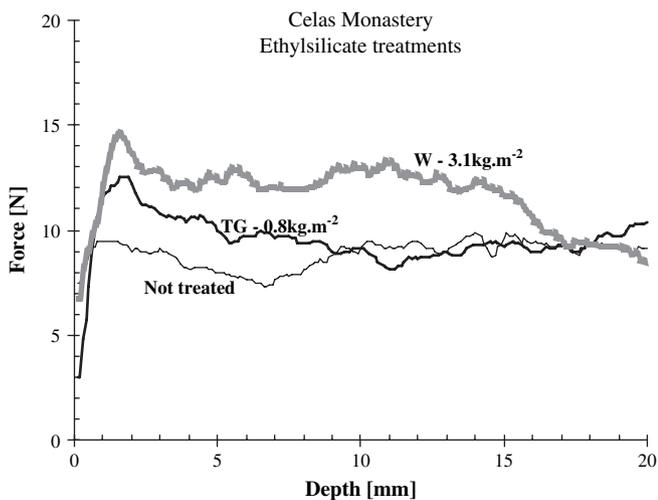


Fig. 9. Drilling resistance in a column of Celas Monastery before and after treatment with two commercial ethyl silicates. Each drilling graph is the average value of at least two holes.

respective technical sheets. In this specific test, the drilling resistance was measured with a 5 mm diamond drill bit under the following drilling conditions: 300 rpm and 20 mm min^{-1} . As can be observed, the behaviour tested in real conditions confirmed the influence of the amount of product in the consolidation action promoted by ethyl silicate consolidants and in the thickness of stone that became consolidated. Again, the poor consolidating capacity of ethyl silicate consolidants is reflected in the apparent small strength increase of the consolidated stone layer.

For the stones able to absorb consolidating products in sufficient amounts, the results demonstrate the importance of specifying the amount of product that must be involved in a consolidation treatment to achieve the desired penetration depth and resistance increase.

4.2. Number of applications

The procedures adopted for brushing application have an important incidence in the total amount that can be used in

a stone treatment. Fig. 10 shows the results obtained with the specimens treated by brushing. A second application in the same day means that 4 h of rest have elapsed after the first one. These results show that after the first application the absorption capacity of the stone were significantly modified. After the first application it was never possible to apply amounts of product similar to those consumed in the first action. They also show that higher amounts of product can be applied when the application consists of a single albeit longer operation.

Fig. 11 presents and compares the values of the amount of product TG and B consumed in the laboratory and on some test areas in Celas Monastery, Coimbra University, Sub-Ripas Palace and S. Julião Fortress following the same protocol in all the applications. All the amounts of product evaluated and plotted in Fig. 11 are expressed as Q_i/Q_1 , the ratio of the amount of product consumed in each application (Q_i) to the amount of product consumed in the first application (Q_1). As can be observed, the practical experiments performed on-site corroborate the laboratory conclusions in terms of the influence of the number of applications in the amount of product consumed for brushing applications.

On site other treatments by brushing for different periods elapsed between applications were also carried out. All the protocols tested for TG consisted of four applications, two on the first day of the treatment plus another two on another

day. The time between applications of TG in the same day is variable, as well as the number of days elapsed between the first and the second days of treatment. As regards the different protocols tested for product B, all of them consisted of two applications in the same day varying the number of hours between the first and the second application. Fig. 12 shows the amounts of product consumed for the different protocols tested on site for products TG and B. All the amounts of product evaluated are expressed as the ratio Q_i/Q_1 of the amount of product consumed in each application (Q_i) to the amount of product consumed in the first application (Q_1). It would be expected that the increment of the time interval between applications would create conditions for the supports to absorb larger amounts of products, but the results obtained do not indicate any significant increase of the absorption capacity, thus confirming the inability to apply in a second trial an amount similar to that consumed in the first application.

Snethlage and collaborators [18] pointed out that the highest strength increase that can be obtained by a silica ester consolidation product is promoted by the first application and to a lesser degree by the second one. The third and fourth applications do not further significantly increase the final strength. These authors consider that the SiO_2 gel formed during the first and second applications are precipitated in the small pores causing strengthened grain–grain-contacts, while the SiO_2 gel from further applications is precipitated in the coarser pores,

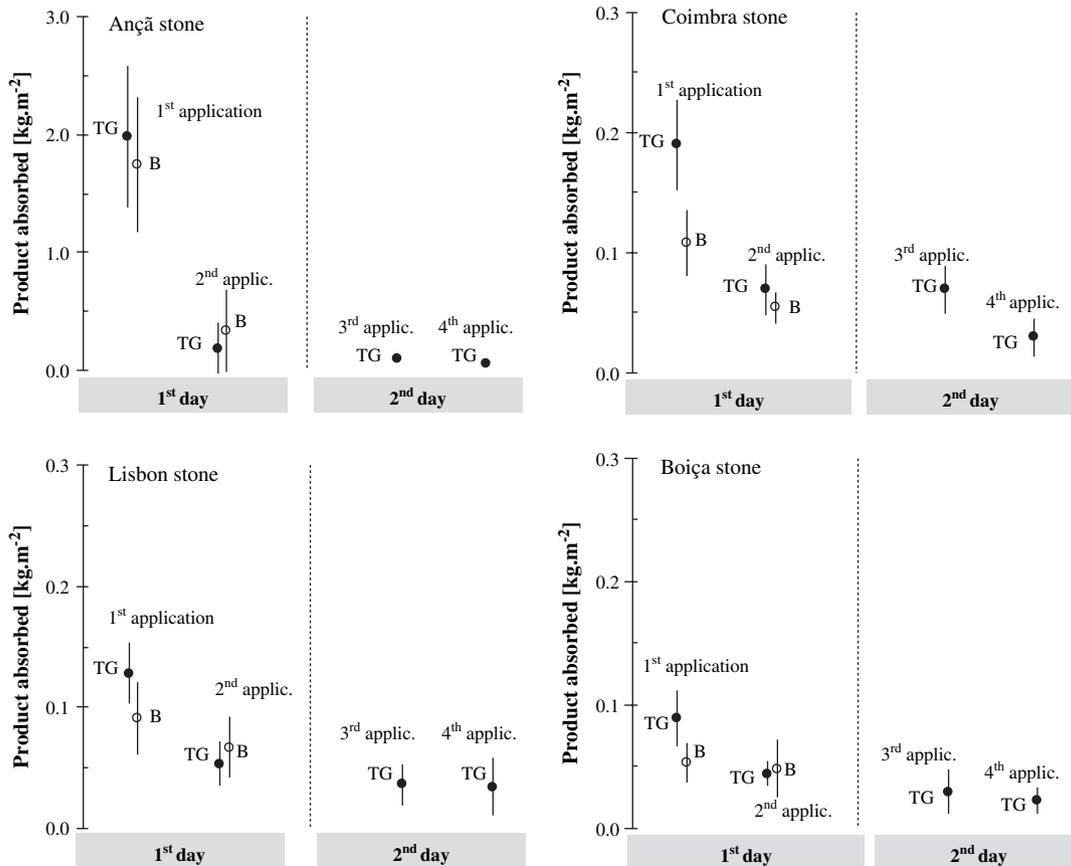


Fig. 10. Variation of the amounts absorbed with the number of applications for consolidation treatments made by brushing with ethylsilicate (filled symbols) and acrylic resin (empty symbols).

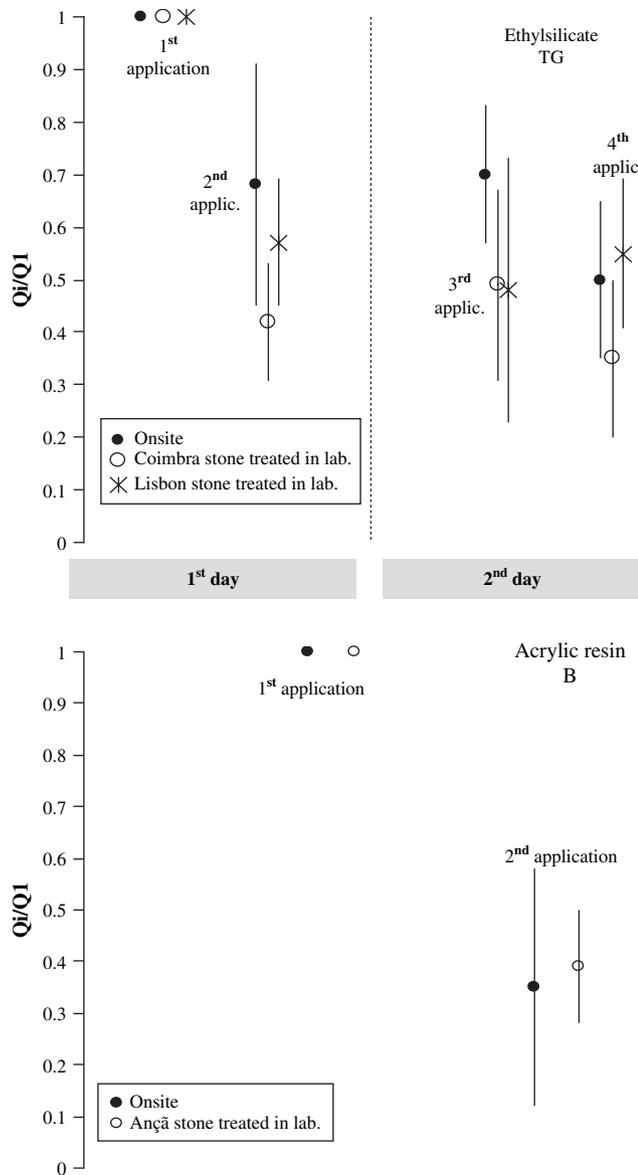


Fig. 11. Comparison of results obtained in laboratory and in onsite conditions showing the influence of the number of applications on the amount of product consumed.

where only empty space is filled, but no strength is gained. In complement to the conclusions of these authors, our results also show that there is a significant reduction of the stone absorption capacity after the first application, possibly due to changes in the pore space induced by this first application, thus limiting the consolidating effect of the successive trials.

4.3. Time and process of immersion

The time of immersion is a parameter that must be taken into consideration when performing consolidation treatments by immersion. The form and dimensions of specimens as well as the time of immersion influence decisively the total amount of product remaining inside and consequently the induced consolidation action. Fig. 13 indicates that the time of

immersion is relevant in all lithotypes and show that 3 h is sufficient to introduce a very significant amount of product in the more porous stones when compared to the amount absorbed in the longer immersion period (values from 60% to 85% and from 70% to 95%, respectively for Ançã and Coimbra stones).

To better define the immersion protocol, two distinct immersion procedures were tested. To obtain a better discrimination in the results, only the more porous stone (Ançã) was tested. Five specimens were used in each experiment. Specimens were left lying horizontally on glass rods and absorbing the product for 24 h (14 h for EP).

In the immersion type “a”, specimens were immersed for 2/3 of their thickness, left to absorb until the capillary fringe reached the top for the epoxy resin and for 14 h in the other two products; then specimens were turned upside down and submerged completely and left immersed until the end of the immersion period (14 h and 24 h). To respect the immersion geometry, after immersion the specimens were kept under laboratory conditions in the horizontal position with the respective faces in the position they had in the first immersion step.

In the immersion type “b”, specimens were let to absorb the product by capillarity contact until the uptake fringe reached the upper face. At that instant, specimens were fully immersed and let to absorb until the end of the period (14 or 24 h). After immersion, specimens were kept in lab conditions in a vertical position.

The influence of the immersion procedure was evaluated through some mechanical and physical characteristics. Table 6 and Fig. 14 show the increase in ultrasonic velocity and flexural strength for the two immersion procedures. Figs. 15 and 16 show the results of drilling resistance and microdrop absorption time. Immersion type “b” was responsible for the highest increases in ultrasonic velocity, flexural resistance and drilling resistance. The differences between the increase of the mechanical strength obtained with ethyl silicate (TG) by immersion “a” (83%) and “b” (104%) reveal the dependence of the consolidation on the procedure. The differences in the drilling energy induced by the ethylsilicate (TG) in the immersion types “a” (39%) and “b” (71%) confirm them. These results corroborate the importance of the treatment procedure, even for this process of full immersion that can be considered a simple and straightforward method.

The superficial water absorption characteristics of Ançã stone after immersion “a” suggest that this procedure might have induced a non-homogenous consolidation action for EP and especially for B products. Fig. 16 presents the results of the determination of microdrop absorption time performed on the face of the specimens that in the first phase of the application procedures were placed upwards and on the opposite face. The water microdrop absorption was adapted from the test method RILEM II.8 [37] according to the procedure described elsewhere [38]. As can be observed, the highest reduction in water absorption occurred for products B and EP on the faces of the specimens that in the first phase of immersion “a” were placed upwards and that were more exposed to evaporation after treatment. These results clearly show that the procedures

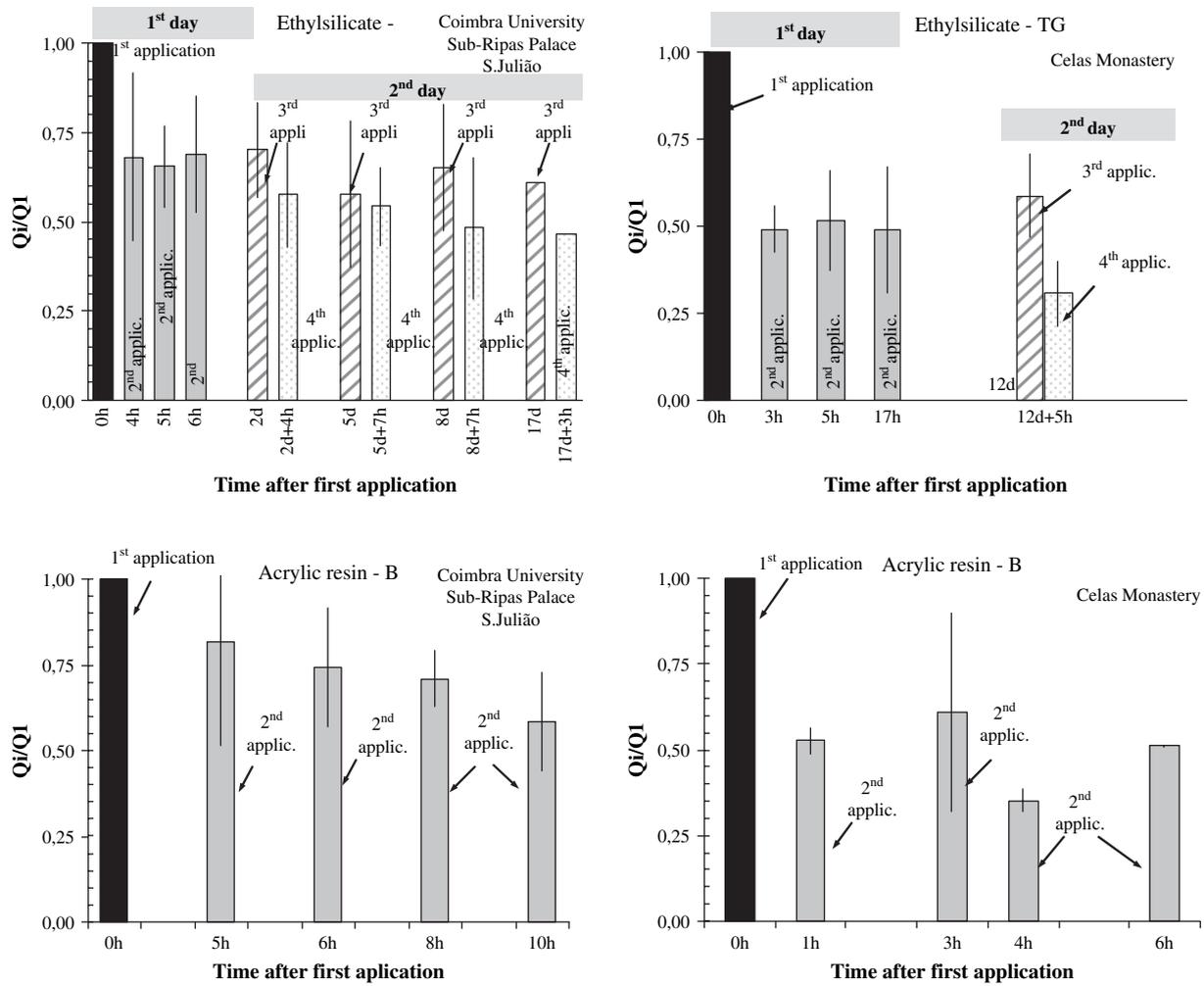


Fig. 12. Influence of the time interval between the first and the subsequent applications in on site tests carried out with products TG and B. In abscissas is the time elapsed since the first application. In the third applications of TG no discrimination of the time of the second application was made, assuming that the influence of that time is irrelevant.

adopted for carrying out the impregnation by immersion and the conditions prevailing during the evaporation of the solvents influence the pattern of the consolidation action. When the evaporation of the solvents occurs preferentially through

some of the faces, a higher consolidation action may develop in the vicinity of these faces, inducing a heterogeneous pattern of the consolidation action.

5. Conclusions

When studying stone consolidation, it is important to have the opportunity to confront data with experience developed by other researchers. Those who have tried to do it know that very seldom were they able to find cases that offer total reliability

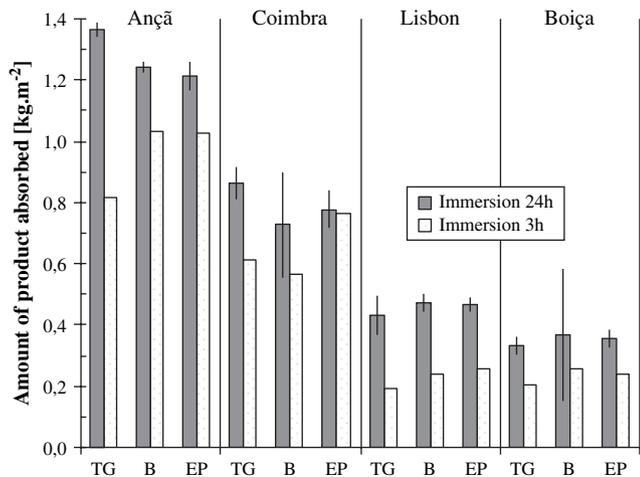


Fig. 13. Consolidation by immersion. Amount of product absorbed in short (3 h) and long term (24 or 14 h) immersion periods.

Table 6 Influence of the immersion procedure on the consolidation action of Ançã stone

Immersion procedure	Ultrasonic velocity increase (%)			Flexural strength increase (%)		
	TG	B	EP	TG	B	EP
a	10 (±2)	9 (±1)	13 (±1)	83	Not determined	
b	17 (±1)	13 (±2)	16 (±3)	104	154	223

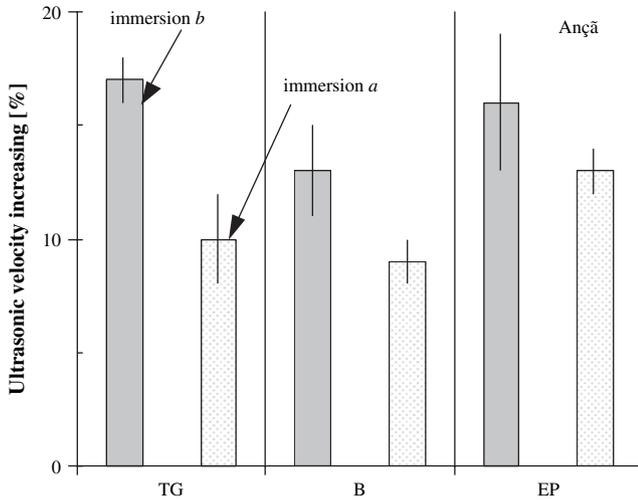


Fig. 14. Ultrasonic velocity increase for Ançã specimens treated through immersion types “a” and “b”.

and which correspond to situations that are really comparable. The results obtained with the series of parametric tests carried out in our research on four different carbonate stones show that this difficulty is justified by the large influence that some apparently minor testing conditions may play in the final test results.

It is easily accepted that the effectiveness of consolidation is a direct function of the amount of product absorbed by the stone, and this assertion was clearly demonstrated with data obtained with the DRMS, namely in terms of the drilling force and of the drilling energy. Accepting that the total amount of product absorbed is a key parameter, our research headed towards identifying the factors that influence the amount of product that a stone specimen or onsite area can absorb and retain.

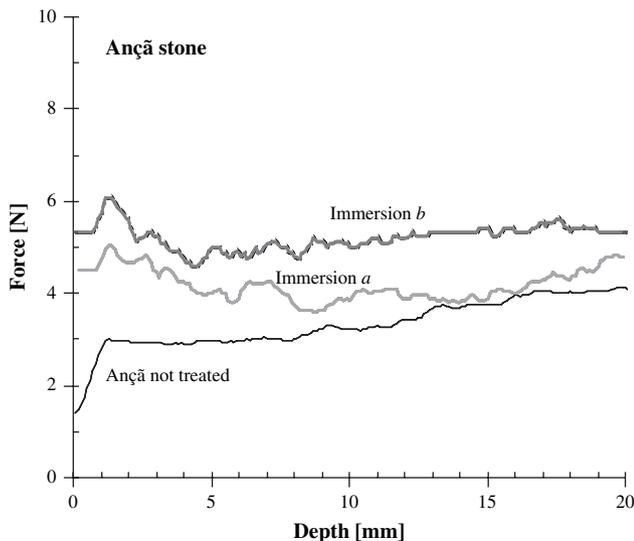


Fig. 15. Drilling graphs of Ançã stone not treated and treated with ethylsilicate (TG) by immersion under conditions “a” and “b”.

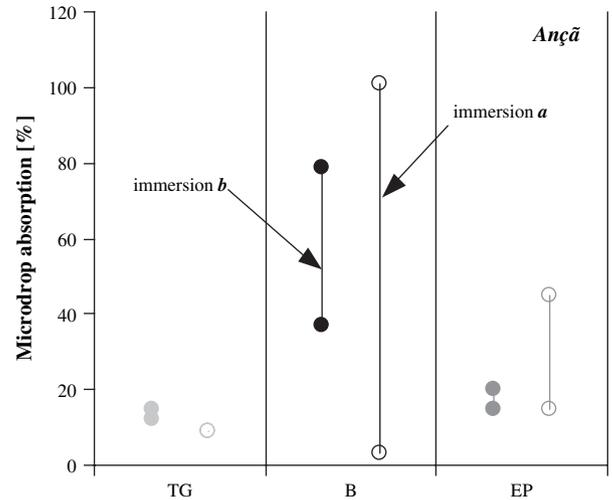


Fig. 16. Microdrop absorption time on two longitudinal and opposite faces of specimens treated by immersion “a” (empty circles) and “b” (filled dots).

The application procedure is known to influence the consolidation performance and many researchers have chosen the application by brushing for its closer proximity to the real practice. Yet, no precise indications are usually provided in terms of the application details. Data presented here show that even minor conditionings may have relevant implications. The first brushing strokes play a decisive role in the final result and this role declines rapidly for the second and subsequent applications. It would be expected that the increment of the time interval between applications would create conditions for the supports to absorb larger amounts of products, but the results obtained do not indicate any significant increase of the absorption capacity, thus confirming the inability to apply in a second trial an amount similar to that consumed in the first application. When a given amount of product is specified to be reached in order to achieve a desired penetration depth and resistance increase, then the operation has to define a proper treatment strategy based mainly on the first application step.

The amount of product absorbed depends strongly on the stone porosity and our results show that it is extremely difficult to treat carbonate stones with porosity lower than around 18%. Above this value, the amount of product absorbed under similar conditions is approximately directly proportional to the porosity value.

In the very porous carbonate stones, acrylic and epoxy resins form thin and hard consolidated layers, peaking at a few millimetres depth, while the ethyl silicate promotes a deeper consolidation although of a very small magnitude. The DRMS drilling profiles show a strong peak for the former and a broad slightly stronger band down to one centimetre or more. When expressed as the drilling energy computed for a fixed drilling length, and for the range of the applied amounts, the consolidation promoted is an approximately linear function of the amount of product retained inside the stone.

The on-site tests carried out have corroborated the main conclusions drawn from the laboratory tests. As an additional

outcome of this research, it became clear that relevant differences between the amount applied (consumption of product) and the amount absorbed may occur, a fact that may be significant when prescribing a treatment in practice.

Application of consolidating products by immersion was studied for different protocols and the results show that slight differences in the treatment procedure influence the homogeneity and the amplitude of the consolidation action.

Acknowledgements

DGEMN, IST and LNEC financially supported this work under the project “Conservation of carbonate stones. Study and selection of treatments”. The authors are grateful to Dr Dória Costa who carried out the drilling resistance measurements on Celas Monastery and to Amélia Reis for her help in the execution of the treatments on site. The first author acknowledges the support of FEDER and Fundação para a Ciência e Tecnologia through the funding of the research unit ICIST, Instituto de Engenharia de Estruturas, Território e Construção. English revision by George Scherer is gratefully acknowledged.

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