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# Evaluation of the effectiveness of treatment products in improving the quality of ceramics used in new and historical buildings

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# ABSTRACT

Ceramic samples made with a mixture of 70% ball clay and 30% guartz sand were moulded and then fired at 900 °C in an electric kiln. Samples were then treated with different products and analyses and tests were performed to evaluate the physical changes induced by the application of these products and their effects on the quality of the ceramics. A petrographic study indicated that the ceramics were composed of quartz, small amounts of mullite and sanidine and traces of hematite. Mineral clays (i.e. kaolinite) disappeared during firing. Two consolidating products (Paraloid B72 and Tegovakon V) and one water repellent (Silo 111) were applied to samples by capillarity, and physical changes (colour, water flow, porosity and pore size distribution) were measured. Finally, we carried out salt crystallization tests in order to determine which product improved the quality of the ceramics. Treated samples registered a decrease in porosity and a general increase in pore size. The application of Silo 111 drastically reduced water absorption by immersion and by capillarity. This product was also responsible for a decrease in pore interconnection. Samples treated with Tegovakon V performed better in terms of their overall hydric behaviour. Silo 111 was the only product that did not modify the colour of samples when compared with untreated ones, and after accelerated aging tests, samples treated with this product hindered the absorption of saline solution into ceramic pores and prevented their decay. Paraloid B72 did not improve any of the properties of the ceramics.

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# 1. Introduction

Modern ceramic production essentially follows the traditional procedure used for thousands of years: a selected clayey material is kneaded with water, the clay is worked into the desired shape, and the piece is then left to dry before being fired in a kiln. Each of these different stages affects the quality of the final product, as many of the defects in finished fired wares, bricks and other ceramics are due to mistakes or failures in one or more of these processes [1,2]. Although the composition of the raw material is the main factor affecting the characteristics of the finished ceramic, the firing temperature is also very important [3]. This is because the changes brought about by firing, which transforms a malleable piece of clay into a hard, finished ceramic, may not occur if the right firing temperature is not reached. During the firing process, the crystal structures start to break down as their stability limits are exceeded and new mineral phases grow following in some cases epitaxial nucleation, which is a more favourable energetic process [4,5]. Moreover, the reaction textures produced by firing ceramics

are in general very similar to those produced by pyrometamorphism [6].

The mineralogy of the raw material, the firing temperature and kiln atmosphere also affect the porosity of the ceramics and, therefore, their capacity to retain water and their mechanical resistance to stresses [7,8]. The colour is also affected [9]. It is well known that ceramic building materials such as bricks fired at an excessively low temperature, are less resistant and more sensitive to attack by decay agents (e.g., moisture, salts, etc.), so favouring their rapid disintegration [10].

This means that porosity and pore size distribution are key factors in the durability of ceramics [11] and are useful means of evaluating their resistance to decay agents [12]. Bricks and other ceramic materials that have been incorrectly fired or are suffering from decay can be protected against further deterioration by applying a range of treatment products [13]. One example is synthetic polymers, which have been widely used as consolidants and water repellents in the conservation of historical buildings since the second half of the 1960's, because they are chemically inert and environmentally stable products that increase the mechanical resistance of the treated materials and/or reduce the amount of water they absorb [14–16].

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| Table 1                        |       |
|--------------------------------|-------|
| General features of treatments | used. |

| Product      | Manufacturer          | Properties      | Dilution         | Composition                        |
|--------------|-----------------------|-----------------|------------------|------------------------------------|
| Paraloid B72 | Rohm & Haas           | Consolidant     | 5% acetone       | Ethyl-methacrylate copolymer       |
| Tegovakon V  | Th. Goldschmidt, A.G. | Consolidant     | 25% ethanol      | Silicic ester with methyl siloxane |
| Silo 111     | C.T.S., S.r.l.        | Water repellent | Includes solvent | Oligomeric organosiloxane          |

The aim of this study is to compare the physical changes that take place when ceramic samples moulded and fired in the laboratory are treated with different treatment products. In this way, we seek to evaluate to what extent these product improve the quality of ceramics and suggest possible new solutions for the conservation of the ceramics used in our architectural heritage.

### 2. Materials and methods

#### 2.1. Preparation of ceramic samples

Ball clay (70 wt.%) from the Abu Sebera quarry (Aswan, Egypt) was mixed with quartz sand (30 wt.%) added as temper. According to Madkour [17], ball clay is chemically rich in SiO<sub>2</sub> (70%), has a considerable  $Al_2O_3$  content (20%) and is poor in Fe<sub>2</sub>O<sub>3</sub> (1.3%), CaO + MgO (1%) and alkalis (0.5%). A sufficient amount of water was added to the raw material to confer plasticity to the mixture and, it was then left for one week to allow the clay particles and ground sand to mix together well, according to the method suggested by Watson [18]. The clayey material was hand-moulded into three different shapes (cubes, tiles and cylinders) using gypsum moulds. The sizes of samples were 3 cm edge for cubes,  $3 \times 3 \times 0.5$  cm for tiles and 3 (height)  $\times$  2.5 (diameter) cm for cylinders. Finally, the samples were dried in the open air and fired in an electrical kiln at 900 °C, one of the most frequently used firing temperatures in the brick industry [7]. This temperature is also ideal for testing the different treatment products, as vitrification of the matrix normally occurs at higher temperatures. Ceramics fired at 900 °C are therefore not so hard and are more vulnerable to decay.

#### 2.2. Treatments application

Two consolidating products (Paraloid B72 and Tegovakon V) and one water repellent product (Silo 111) were chosen. The main characteristics of these products are summarized in Table 1; the percentages of dilution were chosen on the basis of previous experiments [19,20]. Paraloid B72 is an ethyl-methacrylate copolymer used as an adhesive, consolidant and varnish in the conservation of artworks. Various research studies have demonstrated that it is a stable resin for conservation treatments and a preconsolidant agent of porous stones [21,22].

Tegovakon V is an ethyl-silicate specially advised for the consolidation of Si-rich materials (i.e. bricks) with which it has been shown to have good chemical affinity [19], although positive results have also been obtained with calcareous stones [23,24].

Silo 111 is a ready-to-use water repellent for protecting porous materials. It is based on low molecular weight organosiloxane oligomers in 10% dearomatized mineral solvent solution.

Samples were dried for 24 h at  $100 \pm 5$  °C, and then left at room temperature (20 °C) for half an hour, before the products were applied. The solution was absorbed into the samples by capillarity (only the base of the samples was in contact with the solution) for three continuous cycles of 2 hours each with a gap between each cycle of about half an hour. When the products are used "in situ" in the conservation of historical buildings, they, clearly, cannot be absorbed by capillarity and are normally applied by brush or spray gun. Despite this, in our laboratory experiments, we decided

to use capillary absorption because it ensures a more uniform distribution and a better absorption of the products in the ceramics [25]. This means that the results will not be influenced by different amounts of product being applied to one sample or another, or on one face or another in the same sample. The samples were weighed every day to monitor the polymerization process and to ensure that it was fully completed. After the first (Paraloid B72) and the second day of polymerization (Tegovakon V and Silo 111) at laboratory temperature ( $20 \pm 5$  °C), the samples almost reached their final weight (part b of Fig. 1). Those treated with Tegovakon V showed the highest weight increase after the evaporation of solvent (8.91%). Evaporation was continuous but not linear and this produced some flexures in the curves (after the first, the second and the fourth days). This may depend on the modification of the pore network during the polymerization of the products and the simultaneous evaporation of the solvents [26]. Ceramics treated with Paraloid B72, which absorbed a similar amount of product as those treated with Silo 111 (part a of Fig. 1), showed a higher evaporation of solvent. The weight increase of Silo 111 and Paraloid B72 was respectively 2.89% and 1.18%.

After the polymerization of the products, a group of cylindershaped ceramics was sectioned along their height (i.e., parallel to the direction of capillary rise) to see if there were any macroscopic changes in the texture and in the colour. It is interesting to note that the cut surface of samples treated with Tegovakon V was smoothed, whereas it was coarse with the other two products. We observed a totally uniform colour in all sections and the only samples in which water drops were not absorbed were those treated with Silo 111, in which a high contact angle, typical of hydrophobic surfaces, was maintained.

#### 2.3. Experimental techniques

Different analytical techniques were performed to characterize the mineralogy, texture and physical properties of the ceramics and to evaluate the effectiveness of each product. X-ray diffraction analysis (XRD) was performed to identify the mineralogy of both the raw material and the fired ceramic samples using a Philips PW-1710 diffractometer with automatic slit, CuK  $\alpha$  radiation ( $\lambda$  = 1.5405 Å),



**Fig. 1.** Weight variation  $(\Delta M/M)$  of ceramic samples during treatment application by immersion for three cycles of 2 hours each with a gap between each cycle of about half hour (a) and during polymerization (b).

40 kV, 40 mA, 3 to  $60^{\circ}2\theta$  explored area and  $0.01^{\circ}2\theta$  s<sup>-1</sup> goniometer speed. Data were interpreted using the XPowder software package [27].

The texture of the ceramic samples was determined by an Olympus BX-60 polarized optical microscope equipped with a digital microphotography unit (Olympus DP10), while the microtexture of samples and the degree of penetration of the consolidants after treatment was observed using a Leo 1430VP Variable Pressure Scanning Electron Microscope (VPSEM) coupled with EDX microanalysis INCA 350 version 17 Oxford Instrument. Images were acquired in back-scattered (BSE) and secondary electron (SE) modes using polished thin sections and small carbon-coated sample pieces ( $5 \times 5 \times 3$  mm in size).

In order to evaluate how the treatments modified the compactness of the ceramics, ultrasounds were measured on untreated samples using a Steinkamp BP-5 apparatus and then again after the polymerization of products. The propagation velocity of compressional (V<sub>P</sub>) pulses was measured in accordance with the ASTM D 2845 standard [28] for dry test samples using transducers of 100 kHz. A viscoelastic couplant was used to ensure good coupling between transducers and ceramic specimens and the transmission method was used.

Water absorption [29], drying [30] and capillary tests [31] were carried out in order to assess the hydric behaviour of the treated and untreated ceramic samples. The samples used in the absorption and drying tests were cube-shaped, whereas cylindrical samples were used in the capillarity test. Three samples were analysed for each treatment product. Free (A<sub>b</sub>) and forced (under vacuum) water absorption (A<sub>f</sub>), pore interconnection (A<sub>x</sub>) [20], open porosity (p<sub>o</sub>), saturation coefficient (S), drying index (Di), capillarity coefficient (C<sub>C</sub>) and apparent ( $\rho_b$ ) and real densities ( $\rho_{sk}$ ) [32] were calculated as follows:

$$\mathsf{A}_{\mathsf{b}} = \frac{M_L - M_0}{M_0} \times 100,$$

where  $M_0$  is the mass of the dried sample and  $M_L$  is the mass of the sample saturated with water at atmospheric pressure (until constant mass is reached);

$$\mathsf{A}_{\mathrm{f}} = \frac{M_{\mathrm{s}} - M_{\mathrm{0}}}{M_{\mathrm{0}}} \times 100,$$

where  $M_S$  is the mass of the sample saturated with water under vacuum;

$$\mathbf{p}_{\mathrm{o}} = \frac{M_{\mathrm{S}} - M_{\mathrm{0}}}{M_{\mathrm{S}} - M_{\mathrm{H}}} \times 100,$$

where  $M_H$  is the mass of the sample saturated with water under vacuum and weighed in water;

$$A_{\rm x} = \frac{A_f - A_b}{A_f} \times 100;$$

$$S = \frac{M_{48h} - M_0}{M_S - M_0} \times 100,$$

where  $M_{48h}$  is the mass of the sample after 48 hours immersion in water at atmospheric pressure;

$$\mathrm{Di} = \frac{\int_{t_0}^{t_f} f(M_t) \ dt}{M_S \times t_f},$$

defined as the definite integral of the drying curve from the beginning ( $t_0$ ) to the end ( $t_f$ ) times of the test in which  $M_t$  represents a decreasing water weight content starting from the saturation values (under vacuum) as a function of time;

$$C_{\rm C} = \frac{M_{\rm C} - M_0}{A\sqrt{t}},$$

where  $M_C$  is the amount of water absorbed at time *t* and *A* is the surface of the sample in contact with the water;

$$\rho_{\rm b} = \frac{M_0}{M_S - M_H};$$
$$\rho_{\rm sk} = \frac{M_0}{M_0 - M_H}$$

Differences in pore size distribution and in open porosity between untreated and treated samples were determined by mercury intrusion porosimetry (MIP), using a Micromeritics Autopore III porosimeter, model 9410, which can generate a pressure of 414 MPa, covering the pore diameter range from approximately 0.03 to  $360 \,\mu$ m.

The variations in colours before and after the treatment of samples were determined on tile-shaped samples by using a Minolta CR-210 portable colorimeter. The light source chosen was C, which simulates daylight with a temperature colour of 6774K. The overall colour difference ( $\Delta E$ ) in the ceramics caused by these products was quantified as follows:

$$\Delta \mathbf{E} = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2},$$

where  $L_1^*$ ,  $a_1^*$  and  $b_1^*$  are respectively the lightness and the chromatic coordinates of the untreated samples, and  $L_2^*$ ,  $a_2^*$  and  $b_2^*$  those of the treated samples.

Accelerated aging tests were carried out on cube-shaped samples to evaluate the damage produced by salt crystallization in pores and/or fissures of the ceramics. Deterioration of the samples was monitored by visual inspection (i.e., cracking, disintegration and variations in the colour of samples) and weight changes. In accordance with the UNI-EN 12370 standard [33], ten cycles of salt crystallization were performed, using a solution of 14%  $Na_2SO_4 \times 10 H_2O$ .

#### 3. Results and discussion

#### 3.1. Mineralogy and texture

X-Ray diffraction showed that the ball clay used to prepare ceramic samples was mainly composed of quartz but also contained kaolinite, confirming the chemical composition described above. Small amounts of hematite and microcline were also detected. After firing at 900 °C, some changes were detected in the mineralogy of the ceramics: kaolinite disappears, hematite is still distinguishable and quartz from both the ball clay and the sand maintains its high concentration. Two new phases appear, albeit in small amounts: mullite from the decomposition of kaolinite and sanidine from the collapse of microcline.

As regards the texture, the temper is composed of quartz grains with rounded to sub-rounded morphology, wavy extinction and variable size ranging up to 1 mm (Fig. 2a). A few Fe oxides/hydroxides were observed dispersed in the dark-brownish matrix (Fig. 2b). These were probably hematite, as XRD results suggest. Small phyllosilicate pseudomorphs were also observed. Their laminar habit is maintained but birefringence values are low. They may have been transformed into mullite [5] as indicated by XRD analysis. Pores were rounded and elongated in shape and homogeneously distributed in the ceramic matrix.

VPSEM observations showed no signs of vitrification in the texture of the ceramics (Fig. 3a). EDX analyses confirmed the presence of hematite, and also of rutile which had not been detected previously, due to its low concentrations (see EDX spectra in Fig. 3a).

The VPSEM technique was also used to observe the degree of penetration of the treatment products inside the pores of the samples. As regards Paraloid B72, it showed a weak penetration that



Fig. 2. Photomicrograph of fired ceramic sample showing the heterogeneity of quartz grain sizes and rounded pores distributed inside the matrix (a); detailed image showing small Fe-oxide grains (probably hematite) dispersed inside the matrix (b).



Fig. 3. a: BSE image of untreated ceramic showing the presence of oxide crystals of up to 20  $\mu$ m and larger sub-rounded quartz crystals. EDX analyses of hematite and rutile crystals are reported; SE images of samples treated with Paraloid B72 (b), Tegovakon V (c) and Silo 111 (d).

only favours the formation of a thin superficial layer after solvent evaporation (Fig. 3b). In fact, this was the treatment that least affected the weight of the ceramics (Fig. 1). Tegovakon V and Silo 111 products penetrated more deeply inside the samples (Fig. 3c and d).

# 3.2. Degree of compactness

The mean velocity in untreated ceramics was 1688 m/s (Table 2), which confirms that these pieces are not very hard. In fact, highly vitrified ceramics collected from monuments [34] or moulded and fired in the laboratory [35] can reach velocities of 3000 m/s or higher. After polymerization, all ceramics showed an increase in

#### Table 2

Average velocities for the propagation of ultrasonic V<sub>P</sub> pulses (in m/s) of untreated ceramic samples and samples treated with Paraloid B72, Tegovakon V and Silo 111. Standard deviation ( $\sigma$ ) and variation of velocity after the polymerization of products ( $\Delta$ V<sub>P</sub>, in %) are indicated.

|              | Untreated | Paraloid B72 | Tegovakon V | Silo 111 |
|--------------|-----------|--------------|-------------|----------|
| VP           | 1688      | 1794         | 1894        | 1744     |
| σ            | 15.87     | 19.00        | 16.70       | 11.14    |
| $\Delta V_P$ | -         | 6.28         | 12.20       | 3.32     |

velocity whatever product was used (Table 2). These increases were as follows: 12.2% for samples treated with Tegovakon V, 6.28% for samples treated with Paraloid B72 and 3.32% for samples treated with Silo 111. These results reflect the specific function of the products: Tegovakon V and Paraloid B72, whose function is to consolidate the ceramic, increased its toughness; while Silo 111, whose function is to protect the ceramic from water without improving its mechanical qualities, produced a relatively low increase in its compactness.

# 3.3. Hydric tests

There were significant differences between the treated and untreated specimens in terms of hydric behaviour. The samples treated with Paraloid B72 absorbed almost the same amount of water as untreated samples (~14%, Fig. 4 and Table 3), probably because of its low penetration inside the ceramic. This product is a consolidant and not a water repellent and its function is to improve the mechanical qualities. As was expected, in products treated with Silo 111, only 3% of water was absorbed (Fig. 4 and Table 3), whereas the water absorbed by samples treated with Tegovakon V was about 9.7%. When samples were submitted to forced water absorption, we observed that those treated with Silo 111 reached the highest



**Fig. 4.** Free water absorption, forced water absorption and drying curves for untreated samples and samples treated with Paraloid B72, Silo 111 and Tegovakon V. Weight variation ( $\Delta$ M/M) versus time (in hours).

Ax value (45.22, Table 3). This means that the product drastically reduces the interconnection between the pores. The other products provide lower Ax values (ranging between 1.25 and 3.63, Table 3), which indicate a much better pore interconnection. The saturation coefficient (S, Table 3) is directly related to the interconnectivity of the pores and was highest in the untreated samples and decreased when the products were applied, especially with Silo 111. The untreated samples were the fastest to dry, followed by the samples treated with Tegovakon V, Paraloid B72 and, finally, Silo 111 (Di, Table 3). If we analyse the slope of drying curves in more detail, we find that all specimens are characterized by an initial "constant rate drying" [36], in which water evaporation is constant, and occurs by diffusion of vapour from the wet surface to the environment. The process is not affected by the structure of the ceramic. This first stage only occurs quickly in ceramics treated with Silo 111, while it takes longer in the other ceramics, and is slowest in untreated samples. The drying rate changes when the "critical moisture content" is reached and water loss now depends on the movement of water vapour from the pores to the surface ("falling rate drying" [36]). In this second phase, liquid movement occurs by capillarity and is influenced by the radii of the pores [37]. Notice how this second stage is similar in samples treated with Paraloid B72 and Tegovakon V. This is confirmed by their similar capillarity coefficient values (Cc, Table 3). As regards this last parameter, untreated samples absorbed water by capillarity faster than treated ones and Silo 111 stood out for its very low values, confirming its effectiveness as a water repellent.

Samples treated with Paraloid B72 achieved almost the same value for open porosity as untreated samples ( $p_0$ , Table 3) suggesting that this product hardly penetrated the ceramics, while the other two products showed a fall in this value, especially Silo 111 which reached just 11%.

#### Table 3

Hydric parameters of untreated ceramic samples and samples treated with Paraloid B72, Tegovakon V and Silo 111. Each parameter represents the mean value of three samples.

|                | Untreated | Paraloid B72 | Tegovakon V | Silo 111 |
|----------------|-----------|--------------|-------------|----------|
| A <sub>b</sub> | 14.08     | 14.23        | 9.69        | 3.15     |
| A <sub>f</sub> | 14.61     | 14.41        | 9.87        | 5.75     |
| Ax             | 3.63      | 1.25         | 1.82        | 45.22    |
| po             | 27.61     | 27.09        | 19.98       | 10.99    |
| Di             | 0.76      | 0.80         | 0.77        | 0.82     |
| $\rho_b$       | 1.89      | 1.88         | 2.03        | 1.91     |
| $\rho_{sk}$    | 2.61      | 2.58         | 2.53        | 2.15     |
| S              | 94.17     | 89.33        | 87.09       | 13.06    |
| Cc             | 0.201     | 0.106        | 0.110       | 0.004    |

 $\begin{array}{l} A_b \text{: free water absorption (\%); } A_f \text{: forced water absorption (\%); } Ax \text{: pore interconnection (\%); } p_o \text{: open porosity (\%); } Di \text{: drying index; } \rho_b \text{: apparent density (g/cm^3); } \rho_{sk} \text{: real density (g/cm^3); } S \text{: saturation coefficient (\%); } Cc \text{: capillarity coefficient.} \end{array}$ 



Fig. 5. Pore size distribution curves for untreated samples and samples treated with Paraloid B72, Silo 111 and Tegovakon V. Pore radius (in  $\mu$ m) versus log (DV/Dr) (in mL/g).

The real density values ( $\rho_{sk}$ , Table 3) are typical of this type of material and similar to the density of quartz (2.65 g/cm<sup>3</sup>), the main component of the fired samples, while the apparent density ( $\rho_b$ ) is closely linked to the capacity of the ceramics to polymerize the different products. In fact, if we compare these values with the curves in Fig. 1, it is evident that the ceramic that retains the largest amount of product, i.e. the one treated with Tegovakon V, has the highest  $\rho_b$  value, followed by Silo 111 and Paraloid B72, which shows almost the same  $\rho_b$  value as untreated samples.

According to hydric data, the application of Silo 111 offers the greatest protection for ceramic samples when they absorb water by immersion or by capillarity: in fact, free water absorption was ~5 times lower following this treatment and the capillary coefficient was  $\sim$ 50 times lower. Nevertheless, the penetration of this product reduces pore connectivity (high Ax values), preventing the water from flowing quickly through the pores towards the surface as the highest Di value shows. From this point of view, Tegovakon V seems to be the product that achieves the most interesting results overall: ceramics treated with this product absorb less water than untreated samples and than those treated with Paraloid B72; they have a good pore interconnection which favours fast drying especially during the first minutes of the test (Fig. 4) and their Di value is very similar to that of untreated samples; capillarity does not rise as quickly as in untreated samples. Finally, it is the only product whose properties remain unchanged at the end of the test. In fact, samples treated with Paraloid B72 and Silo 111 weighed less than at the beginning of the hydric tests (see the end of the drying curves in Fig. 4), suggesting that part of the product was lost in the water during the analysis (the distilled water was not analysed after the hydric test but no ceramic fragments were detected in the tank).

#### 3.4. Porosimetry

The MIP technique provided a reliable picture of the porosity and pore system of the ceramics and of the changes induced by the application of the different products. Untreated ceramic samples showed a bimodal curve with a main peak at around 0.08  $\mu$ m and a second smaller peak at about 0.5  $\mu$ m (Fig. 5). These pore ranges and porosity values are typical for this type of material when used in monuments and new buildings [38–40]. When samples were treated, pore radii became larger in the range between 1 and 0.1  $\mu$ m (Table 3). Tegovakon V was the only product that brought about a moderate increase in the number of pores with diameters of less than 0.01  $\mu$ m (Fig. 5) probably due to the development of microcracks in the consolidant when it polymerizes in capillaries [26].

#### Table 4

Results of the MIP test on untreated ceramic samples and samples treated with Paraloid B72, Tegovakon V and Silo 111.

|              | <b>p</b> <sub>oMIP</sub> | >10 | 10-1 | 1-0.1 | < 0.1 |
|--------------|--------------------------|-----|------|-------|-------|
| Untreated    | 30.75                    | 3.2 | 4.0  | 43.2  | 49.6  |
| Paraloid B72 | 27.16                    | 2.4 | 8.3  | 57.4  | 32.0  |
| Tegovakon V  | 27.07                    | 3.4 | 3.5  | 53.7  | 39.4  |
| Silo 111     | 19.10                    | 3.8 | 8.4  | 58.2  | 29.7  |

 $p_{oMIP}$ : open porosity (%); relative porosity distribution (%) according to pore sizes ranges (> 10, 10-1, 1-0.1 and < 0.1  $\mu m$ ).

The porosity obtained by MIP for the untreated sample was 30.75%, while the results for samples treated with Paraloid B72, Silo111 and Tegovakon V were always lower (Table 4). Although the MIP results classified the products in the same order (from the most to the least porous) as the hydric tests, the values obtained with MIP were always substantially higher ( $p_0$  and  $p_{oMIP}$ , Tables 2 and 3, respectively).

# 3.5. Colorimetry

The application of Paraloid B72 and Tegovakon V made the ceramics visibly darker, whereas the use of Silo 111 only caused changes that were indistinguishable to the naked eye. Colorimetric analyses showed that the lightness ( $L^*$ ) was lower for samples treated with Paraloid B72 and Tegovakon V, confirming that they were indeed darker (Table 5). As regards chromaticity, the application of Silo 111 left  $a^*$ ,  $b^*$  and  $C^*$  values practically unchanged, compared with untreated samples, while Paraloid B72 caused the greatest colorimetric modifications. As a matter of fact, the colour difference value ( $\Delta E$ ) was almost zero in the case of ceramic treated with Silo 111 and was ten times higher with the application of Paraloid B72 (Table 5).

# 3.6. Salt crystallization test

The salt crystallization test had a considerable effect on the durability of some of the samples investigated because it led several forms of deterioration (cracking, lamination, powdering, even total disintegration) to develop (Fig. 6). Almost all samples showed a slight increase in weight after the first test cycle due to penetration of saline solution within the pores (Fig. 7). The samples treated with Paraloid B72 achieved the worst results throughout this test. In fact, after the 2nd cycle, they began to crumble. After the 5th cycle, one of the ceramics treated with this product totally disintegrated. At the end of the test, the mean weight loss was 77.86%, a value higher than that for untreated samples, which behaved in a similar way but showed a final weight loss of 69.48%.

Tegovakon V also achieved poor results, with cracks developing on the surfaces, which increased its roughness. After the 5th cycle, fragments started to fall off and one sample completely disintegrated after the 8th cycle (Fig. 7). Weight loss was again higher than with untreated samples (77.89%).

The samples treated with Silo 111 showed a very slight weight loss after the 5th cycle, maintaining their shape and weight

#### Table 5

Lightness ( $L^*$ ), chromatic coordinates ( $a^*$  and  $b^*$ ), chroma ( $C^*$ ), hue angle ( $H^\circ$ ) and colour difference values ( $\Delta E$ ) of untreated ceramic samples and of samples treated with Paraloid B72, Silo 111 and Tegovakon V, using illuminant C. Each value represents the mean of six analyses.

|              | $L^*$ | <i>a</i> * | b*    | С*    | H°    | $\Delta E$ |
|--------------|-------|------------|-------|-------|-------|------------|
| Untreated    | 79.04 | 7.18       | 10.58 | 12.78 | 55.80 | -          |
| Paraloid B72 | 69.51 | 10.82      | 14.01 | 17.71 | 52.32 | 10.76      |
| Tegovakon V  | 73.22 | 8.81       | 11.08 | 14.16 | 51.56 | 6.06       |
| Silo 111     | 78.38 | 7.17       | 10.45 | 12.67 | 55.53 | 0.67       |



**Fig. 6.** Appearance of untested control sample and samples altered by ten cycles of the salt crystallization test: a) untested sample; b) altered sample that had not been treated with any product; c) altered sample treated with Paraloid B72; d) altered sample treated with Tegovakon V; e) altered sample treated with Silo 111.



**Fig. 7.** Weight change ( $\Delta$ M/M) in untreated samples and in samples treated with Paraloid B72, Tegovakon V and Silo 111 during salt crystallization cycles.

without any alteration until the end of the test (Figs. 6 and 7). The weight loss was 0.58%. Due to its hydrorepellent properties, the application of this product hindered the absorption of saline solution into the ceramic body. In monuments in which the brick has been damaged by the presence of salts, similar efficiency has been observed in situ when water repellent products, sometimes mixed with consolidants, were applied [41].

#### 4. Conclusions

The following conclusions can be drawn from the data we obtained:

- no evidence of vitrification was observed in ceramic samples fired at 900 °C. Few mineralogical changes were detected: these included the disappearance of kaolinite and microcline and the crystallization of mullite and sanidine;
- the measurements of weight change in the ceramics after the application of the products, and the VPSEM observations both demonstrated that Tegovakon V achieved the best degree of penetration inside the ceramics, whereas Paraloid B72 achieved only slight penetration. As regards the increase in the compactness of the ceramics after polymerization with the different products, the lowest increase was when Silo 111 was applied because it is the only non-consolidating product;
- the application of the treatments led to a change in the colour of the samples, except for Silo 111;

- treated samples showed different hydric behaviours depending on the type of product used. Those treated with Paraloid B72 showed similar trends to untreated ones, while samples treated with Silo 111 absorbed less water. However, application of this product reduced pore interconnection sharply leading to a fall in drying speed. When Tegovakon V was applied, samples did not absorb very much water, pore interconnection was maintained and the samples dried faster than the other treated samples. Moreover, Tegovakon V was the only product whose properties remained unaltered over the time required to carry out the hydric test;
- the application of any of the products being tested led to changes in the pore system and a reduction in open porosity;
- the samples treated with Paraloid B72 and Tegovakon V achieved bad results in the salt crystallization test because they cracked partially and some of them totally disintegrated. On the other hand, samples treated with Silo 111 only showed a slight weight loss and maintained their shape without any visible alteration;
- if we compare the three products, the results for Paraloid B72 are disappointing, since it only partially consolidated the ceramics and neither the hydric properties nor the durability of the samples studied improved.

This investigation represents a significant contribution to a greater understanding of the damage that can be suffered by ceramics, even when they are treated with consolidants or water repellent products. These results can help restorers to choose the most appropriate product to prevent or reduce the decay of ceramics depending on their physical-mechanical properties and the types of deterioration agent to which they are exposed.

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#### References

- J. Cerdeño del Castillo, R. Díaz Rubio, J. Obis Sánchez, A. Pérez Lorenzo, J. Velasco Vélez, Manual de patologías de las piezas cerámicas para la construcción, Aitemín, Toledo (Spain), 2000.
- [2] S.S. Singer, F. Singer, Industrial Ceramics, Chapman & Hall Ldt, London (UK), 1963.
- [3] S. Buys, V. Oakley, Conservation and restoration of ceramic, Butterworth-Heinemann, London (UK), 1996.
- [4] A.J. Brearley, D.C. Rubie, Effects of H<sub>2</sub>O on the disequilibrium breakdown of muscovite + quartz, J. Petrol. 31 (1990) 925–956.
- [5] C. Rodríguez Navarro, G. Cultrone, A. Sánchez Navas, E. Sebastián, TEM study of mullite growth after muscovite breakdown, Am. Mineral. 88 (2003) 713–724.
- [6] R. Grapes, Pyrometamorphism, Springer, Berlin (Germany), 2006.
- [7] G. Cultrone, E. Sebastián, K. Elert, M.J. de la Torre, O. Cazalla, C. Rodríguez Navarro, Influence of mineralogy and firing temperature on porosity of bricks, J. Eur. Ceram. Soci. 24 (2004) 547–564.
- [8] J. Warren, Conservation of brick, Butterworth-Heinemann, Oxford (UK), 1999.
- [9] R. Kreymeyer, Some notes on the firing colour of bricks, Appl. Clay Sci. 2 (1987) 175–183.
- [10] R. Carlsson, Mechanisms of deterioration in ceramics and glass, Durability Build. Mater. 5 (1988) 421–427.
- [11] D. Benavente, Why pore size is important in the deterioration of porous stones used in built heritage, Macla 15 (2011) 41–42.
- [12] G. Cultrone, M.J. de la Torre, E. Sebastián, O. Cazalla, C. Rodriguez Navarro, Behaviour of brick samples in aggressive environments, Water, Air Soil Pollut. 119 (1999) 191–207.

- [13] F. Sandrolini, E. Franzoni, Consolidation of ancient architectural materials: performances and reinforcing mechanisms in restoration, in: J.R. Blizzard, H. Garbacz, R. Pielaszek, A. Rytel, A. Szadkowski (Eds.), E-MRS Fall Meeting, Pielaszek Research, Warsaw (Poland), 2006, p. 106.
- [14] M. Lazzari, O. Chiantore, Thermal-ageing of paraloid acrylic protective polymers, Polymer 41 (2000) 6447–6455.
- [15] M.K. Favaro, R. Mendichi, F. Ossola, U. Russo, S. Simon, P. Tomasin, P.A. Vigato, Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: photo-oxidative weathering, Polym. Degrad. Stabil. 91 (2006) 3083–3096.
- [16] M.F. Vaz, J. Pires, A.P. Carvalho, Effect of the impregnation treatment with Paraloid B-72 on the properties of old Portuguese ceramic tiles, J. Cult. Herit. 9 (2008) 269–276.
- [17] F.S. Madkour, Study of technology, treatment and conservation of archaeological ceramic tiles in Egypt with application on some examples from Ottoman period and Mohamed Ali period, Master Thesis, University of Cairo (Egypt), 1999.
- [18] O. Watson, Ceramic from Islamic lands, Thames & Hudson Ltd, London (UK), 2004.
- [19] A. Luque, G. Cultrone, E. Sebastián, O. Cazalla, Effectiveness of Stone treatments in enhancing the durability of bioclastic calcarenite (Granada, Spain), Mater. Construcc. 58 (2008) 115–128.
- [20] G. Cultrone, M.J. de la Torre, E. Sebastián, O. Cazalla, Evaluation of bricks durability using destructive and non-destructive methods (DT and NDT), Mater. Construcc. 53 (2003) 41–59.
- [21] L. Lazzarini, Treatment cards of Venetian monuments and sculptures, 3rd International Congress on "Deterioration and Conservation of Stone", Venice (Italy), 1979.
- [22] J. Durán Suárez, Estudio de consolidantes y protectivos para restauración de material pétreo, PhD. Thesis, University of Granada (Spain), 1996.
- [23] L. Lazzarini, M. Laurenzi Tabasso, Il restauro della pietra, CEDAM, Padova (Italy), 1986.
- [24] E.M. Sebastián, M.J. de la Torre, O. Cazalla, G. Cultrone, C. Rodriguez Navarro, Evaluation of treatments on biocalcarenites with ultrasounds, NDT.net 12 (1999) 10.
- [25] R. Villegas Sánchez, Metodología para la evaluación y estudio previo de tratamientos, Cuadernos Técnicos n.8: Metodología de diagnóstico y evaluación de tratamientos para la conservación de los edificios históricos, Consejería de Cultura, Junta de Andalucía (2003) 194–207.
- [26] M.J. Mosquera, J. Pozo, L. Esquivias, Stress during drying of two stone consolidants applied in monumental conservation, J. Sol-Gel Sci. Technol. 26 (2003) 1227–1231.
- [27] J.D. Martin, XPowder. A software package for powder X-ray diffraction analysis, Lgl. Dep. GR 1001/04, 2004.
- [28] ASTM D 2845-05, Standard method for laboratory determination of pulse velocities and ultrasonic elastic constants of rock, ASTM International Standards Worldwide, Pennsylvania, 2005.
- [29] UNI-EN-13755, Metodi di prova per pietre naturali. Determinazione dell'assorbimento d'acqua a pressione atmosferica, CNR-ICR, Rome (Italy), 2002.
- [30] NORMAL 29/88, Misura dell'indice di asciugamento (drying index), CNR-ICR, Rome (Italy), 1988.
- [31] UNI-EN-1925, Metodi di prova per pietre naturali. Determinazione del coefficiente di assorbimento d'acqua per capillarità, CNR-ICR, Rome (Italy), 2000.
- [32] RILEM, Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods. Commission 25-PEM: Protection et Érosion des Monuments, 175–253, 1980.
- [33] UNI-EN-12370, Metodi di prova per pietre naturali. Determinazione della resistenza alla cristallizzazione di sali, CNR-ICR, Rome (Italy), 2004.
- [34] G. Cultrone, I. Sidraba, E. Sebastián, Mineralogical and physical characterization of the bricks used in the construction of the "Triangul Bastion", Riga (Latvia), Appl. Clay Sci. 28 (2005) 297–308.
- [35] G. Cultrone, E. Sebastián, K. Elert, M.J. de la Torre, O. Cazalla, C. Rodríguez Navarro, Influence of mineralogy and firing temperature on the porosity of bricks, J. Eur. Ceram. Soc. 24 (2004) 547–564.
- [36] R.E. Kirk, D.F. Othmer, Encyclopedia of Chemical Technology. Vol. 9. Drying, Wiley, New York, 2004, p. 93–141.
- [37] G.W. Scherer, Theory of Drying, J. Am. Ceram. Soc. 73 (1999) 3-14.
- [38] M. Setti, A. Lanfranchi, G. Cultrone, L. Marinoni, Archaeometric investigation and evaluation of the decay of ceramic materials from the church of Santa Maria del Carmine (Pavia, Italy), Mater. Construcc. 62 (2012) 79–98.
- [39] M. Maage, Frost resistance and pore size distribution in bricks, Mater. Struct. 17 (1980) 345–350.
- [40] P. Whiteley, H.D. Russman, J.D. Bishop, Porosity of building materials. A collection of published results, J. Oil Colour Chem. As. 60 (1977) 142–150.
- [41] F.J. Alejandre, R. Villegas, Brick durability and conservation treatment (Santa María de Jesús chapel portal, Seville, Spain), Mater. Construcc. 59 (2009) 85–103.