

Consolidation with ethyl silicate: how the amount of product alters the physical properties of the bricks and affects their durability

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ABSTRACT: We evaluated the consolidating capacity of ethyl silicate in three types of bricks fired at 800, 950 and 1100 °C. We chose two concentrations of product, at 25% and 50%, diluting the product in white spirit to estimate whether greater dilution enables the product to penetrate deeper into the bricks, or whether a higher concentration leads to better consolidation of bricks. The application of ethyl silicate caused bricks porosity to decline and their compactness to increase. These changes were more accentuated as the concentration of the product increased. The pore size distribution not changed substantially except that there were fewer of the smallest pores. The color and the lightness of the pieces changed after application of the consolidant, albeit slightly. The durability of bricks improved as manifested by the results of the salt crystallization test. In general, the longest-lasting pieces were those treated with 25% ethyl silicate.

KEYWORDS: Brick; Weathering; Physical properties; Durability

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RESUMEN: *Consolidación con silicato de etilo: como influye la cantidad de producto en las propiedades físicas de los ladrillos y condiciona su durabilidad.* Se ha evaluado la capacidad consolidante del silicato de etilo en tres tipos de ladrillos cocidos a 800, 950 y 1100 °C. Se eligieron dos concentraciones de producto, al 25% y 50%, diluyéndolo en white spirit para estimar si más dilución favorece una penetración más en profundidad del producto o si una mayor concentración produce una mejor consolidación de los ladrillos. El silicato de etilo ha causado una disminución de la porosidad y un aumento de la compacidad de los ladrillos, acentuándose estas modificaciones con mayor concentración de producto. La distribución porométrica no ha cambiado de forma sustancial, disminuyendo los poros más pequeños. Color y luminosidad de las piezas han modificado ligeramente tras la aplicación del consolidante. Los ladrillos consolidados han mejorado su durabilidad frente al envejecimiento acelerado producido por las sales. En general, las piezas más duraderas han resultado ser las tratadas con el 25% de silicato de etilo.

PALABRAS CLAVE: Ladrillo; Envejecimiento; Propiedades físicas; Durabilidad

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1. INTRODUCTION

Ever since ancient times, human beings have tried to protect historic buildings and artworks from decay, which is manifested for example in crumbling on the surface of the masonry, the development of fissures or fractures and the resulting loss of material, or the proliferation of algae, lichens and other organisms that can cause significant alterations in the color (1, 2). In the past, the worst affected pieces were often replaced or occasionally, oils and resins were applied that prevented the damaging effects of water inside the rocks (3, 4). It was not until the early 20th century that chemical companies started making consolidants and water-repellents to help prevent the decay of our architectural heritage. More recently, several nanomaterials have been tested to assess their capacity for consolidating building stones (5).

The purpose of a consolidant product is to improve the cohesion and adhesion between the different elements in the building material. This gives the material better mechanical resistance and alters the porous system, making it difficult for water and salt solutions to penetrate it (6). From a theoretical point of view, it would be best if the consolidant penetrated the material uniformly and that it reached the healthy, undamaged material below the surface so as to ensure a good cohesion between the mineral grains (7). In practice however, the consolidant does not penetrate in the same way in all parts of the material and some areas are left poorly consolidated and with higher levels of porosity, making it easier for the agents of decay to enter the stone. The method used to apply the consolidant is of crucial importance for ensuring good consolidation. Although in small samples or laboratory tests, the product is often applied by capillary absorption or immersion, which provide deeper, more homogeneous penetration (8, 9), this is not feasible for the façade of a building, on which a brush or a spray-painting device must be used. Another factor which must be taken into account and which is no less important is choosing the most effective product. This is because there are many products on the market with different purposes and the mineralogy and porous system of stones and artificial materials such as bricks and mortar also vary a great deal (10).

In this paper we will be studying the efficacy of the consolidants on bricks, one of the most frequently used building materials in human history and still very popular today. The widespread use of bricks in construction is essentially due to the fact that the clayey earth raw material required to make them is easy to find, the fired brick is cheap to produce and has very good physical and mechanical properties in its role as part of a building (11). The fact that bricks are so easy to produce has led to a certain degree of variability in the composition of

the bricks due to the type of raw material used and/or the addition of additives. The texture also varies according to the method used to prepare the brick for firing and according to the firing temperature in the kiln (12–14). In terms of their composition, bricks are generally regarded as silicates given that quartz and phyllosilicates are normally the most abundant minerals in the clay raw materials. Calcite, dolomite and feldspars *s.l.*, and other newly formed silicates that appear in the pieces fired at high temperatures can be identified fairly frequently (15, 16). In view of this mineralogy, the organosilicon consolidants are considered the most suitable for treating Si-rich materials due to their compositional affinity once the product has polymerized (17). The consolidant action is achieved by creating Si–O–Si bonds that precipitate in the pores and the fissures of the brick or stone, forming a reticular structure similar to that of silica and binding the loose grains together (18, 19).

The objective of this research is to assess the efficacy of ethyl silicate (i.e. tetraethyl orthosilicate or TEOS) in the consolidation of the bricks. Ethyl silicate is the most commonly used product in the consolidation of stone, above all those of siliceous composition (20). Although a great deal of research has been done on consolidants in order to determine how effective they are at protecting stone, much less has been done on their effect on bricks (21). More research should also be done on additional aspects such as the amount of consolidant that must be applied. On this question, it has been observed for instance that the ethyl silicate does not manage to penetrate very deeply, due to evaporation of the solvent during the application phase (22, 23) which gives rise during the decay process to thin layers of stone flaking off (24). In order to solve these problems, we decided to dilute the ethyl silicate with solvent and then apply it in two different concentrations, so as to estimate whether greater dilution of the product enables greater penetration or whether the opposite is true and a higher concentration leads to greater consolidation of the material. Our aim was to find out which of the two applications most improves the consolidation of the brick and its durability. To this end, we monitored possible changes in the compactness, the porous system and the color of the materials as well as their resistance to decay when subjected to the salt crystallization test.

2. MATERIALS AND METHODS

Solid bricks with and without additives were used in this research to evaluate the consolidation efficacy of ethyl silicate. 4 cm-edge bricks cubes were made using a clayey sediment dating from the Middle-High Turolian Age. This sediment is located in Jun (Granada, Spain) and is rich in quartz and phyllosilicates. It also contains smaller amounts of

calcite, feldspars and gypsum (25). It is currently used in the production of bricks and tiles. In this research we used two additives, halite and calcined diatomite sludge. Halite is produced by the evaporation of sea water and is used as a food additive, while calcined diatomite sludge is a typical waste product in beer production, in which diatomite is used in the filtration process. Halite can have beneficial effects as an additive in brick production in that it can act as a melting agent, so reducing the manufacturing costs due to the fact that less energy is required to fire the bricks. The use of calcined diatomite sludge as an additive has more to do with the environmental benefits it can bring by helping reuse and dispose of a waste product with few obvious other uses. These additives were added to the clayey material in the following proportions: 30 wt.% of halite and 10 wt.% of diatomite sludge. Samples with and without additives were fired in an electric oven with an oxidizing atmosphere at 800, 950 and 1100 °C. The temperature of 950 °C is one of the most commonly used in industrial brick manufacture. The other two temperatures were chosen so to allow us to study the physical properties of the bricks over a range (300 °C) in which these properties are thought to vary (13, 26). In all, nine types of bricks were tested in this research: they were labeled as J, JS and JD to distinguish respectively bricks with no additives from those with halite and those with calcined diatomite sludge. Each label is followed by a number referring to the firing temperature.

The product applied to the brick cubes was an ethyl silicate (sold under the trade name of ESTEL 1000) and produced by CTS, s.r.l. This consolidant is a ready-to-use colorless liquid with an active content level of 75% diluted with white spirit. We applied two different concentrations of ESTEL 1000 with a higher dilution compared to the original packaged product. 25% and 50% of ESTEL 1000 were diluted with white spirit and applied by brush. Three coats were applied to the six faces of each cube leaving 15 minutes between each application, so as to improve product absorption. Samples were then left in the laboratory for three weeks to ensure that the product polymerized completely.

The pore size distribution, the pore volume, the specific surface area and the density of untreated bricks were compared with those of similar bricks treated with ethyl silicate using a Micromeritics Autopore III 9410 porosimeter (MIP). This apparatus can measure pores with diameters of between 0.003 and 360 µm. Freshly cut sample chips of about 1 cm³ were oven dried for 24 h at 60 °C and then analyzed.

Research has shown that the pore system of bricks is influenced by the degree of vitrification as the firing temperature increases (13). We therefore decided to estimate the degree of vitrification over our temperature range by calculating the amorphous versus

crystal ratio using X-ray diffraction (XRD) and the X Powder X software. This ratio is based on the mean value of the intensities, the standard deviation and the area of crystal reflections (27). To obtain this datum, powder samples with a particle size of less than 0.053 mm were analysed with a Philips X'Pert PRO diffractometer.

Of all the techniques for determining physical properties, ultrasound is particularly attractive due to its non-destructive nature. Measurements were performed in each of the three perpendicular directions of the brick cubes using a Controls model 58-E4800 ultrasound generator with 54 kHz transducers. The pulse propagation velocity was measured in accordance with ASTM D2845 (28) on dry test samples. A viscoelastic couplant was used to ensure good coupling between transducers and samples. These data were used to obtain information on the degree of compactness of samples before and after the application of treatments. Wave velocity was determined under controlled thermohygro-metric conditions (25 °C, relative humidity 50%). The structural anisotropy (ΔM) was calculated as follows [1] (29):

$$\Delta M = \left(1 - \frac{2V_{p2}}{V_{p2} + V_{p3}} \right) \times 100 \quad [1]$$

where V_{p1} , V_{p2} and V_{p3} are the velocities measured in the three orthogonal directions of cubic samples.

The variation in color before and after the consolidation of brick samples was determined using a Konica-Minolta CM 700d portable spectrophotometer according to the EN 15886 standard (30). The light source chosen was D65, which simulates daylight with a color temperature of approximately 6500 K. The overall color difference (ΔE) in the bricks caused by the application of ethyl silicate was quantified as follows [2]:

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

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.

Finally, in accordance with the EN 12370 standard (31), 10 salt crystallization cycles were performed using a 14% $\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$ solution, which can exert a crystallization pressure in confined spaces of 14 MPa (32). This test provided information on the damaging effects of the soluble salts which are usually present in water and can crystallize in brick pores and fissures. Three samples of each brick type were used. The damage produced by the salt crystallization test was evaluated via visual inspection of material loss and weight changes. The damage to the bricks was also monitored by ultrasound.

3. RESULTS

3.1. Porous system

When it comes to evaluating the effectiveness of the ethyl silicate, it is essential to study the porous system of the bricks given that the application of any consolidant product can have a dramatic impact on the porosity and the size of the pores (33). The untreated bricks showed porosity levels of between 38% and 46%, and a unimodal pore size distribution in which the majority of the pores had a radius of around 1 μm . More specifically, in the bricks without additives the porosity accessible to Hg increased slightly between 800 $^{\circ}\text{C}$ (38.3%) and 1100 $^{\circ}\text{C}$ (40.9%) and the maximum pore size also increased slightly from 0.4 to 0.5 μm (Figure 1). The pore size influences the specific surface area (SSA, Table 1) values, which are higher in the pieces fired at 800 $^{\circ}\text{C}$ reaching almost 6 m^2/g before falling back to around 2 m^2/g when temperatures of 950 $^{\circ}\text{C}$ and 1100 $^{\circ}\text{C}$ are reached. The addition of additives leads to certain

changes in the porous system. The open porosity increases above all when calcined diatomite sludge is added (P_o , Table 1), exceeding 46% at 800 $^{\circ}\text{C}$. The SSA values drop as firing temperature increases, which suggests that the smallest pores are disappearing due to the vitrification of the bricks. The vitrification of bricks was confirmed by XRD analysis. In fact, the amorphous versus crystal ratio (a/c , Table 2) gradually increases in line with the increase in the firing temperature in all brick types. In the bricks made with halite, the SSA value at 800 $^{\circ}\text{C}$ is less than 3 m^2/g , while in the other two groups it is over 5 m^2/g . This important difference is due to the fact that this salt acts as a melting agent, precisely at 800 $^{\circ}\text{C}$ (34). The bricks with halite (JS) had the highest a/c ratio at 800 $^{\circ}\text{C}$ (Table 2). JS also had the lowest SSA values at 950 $^{\circ}\text{C}$ and 1100 $^{\circ}\text{C}$, although the differences between JS and the other two groups became narrower as all the pieces started to vitrify (Table 1). Indeed, J and JD fired at 1100 $^{\circ}\text{C}$ seem to have achieved a greater degree of vitrification than JS (Table 2). The bricks with additives also have a

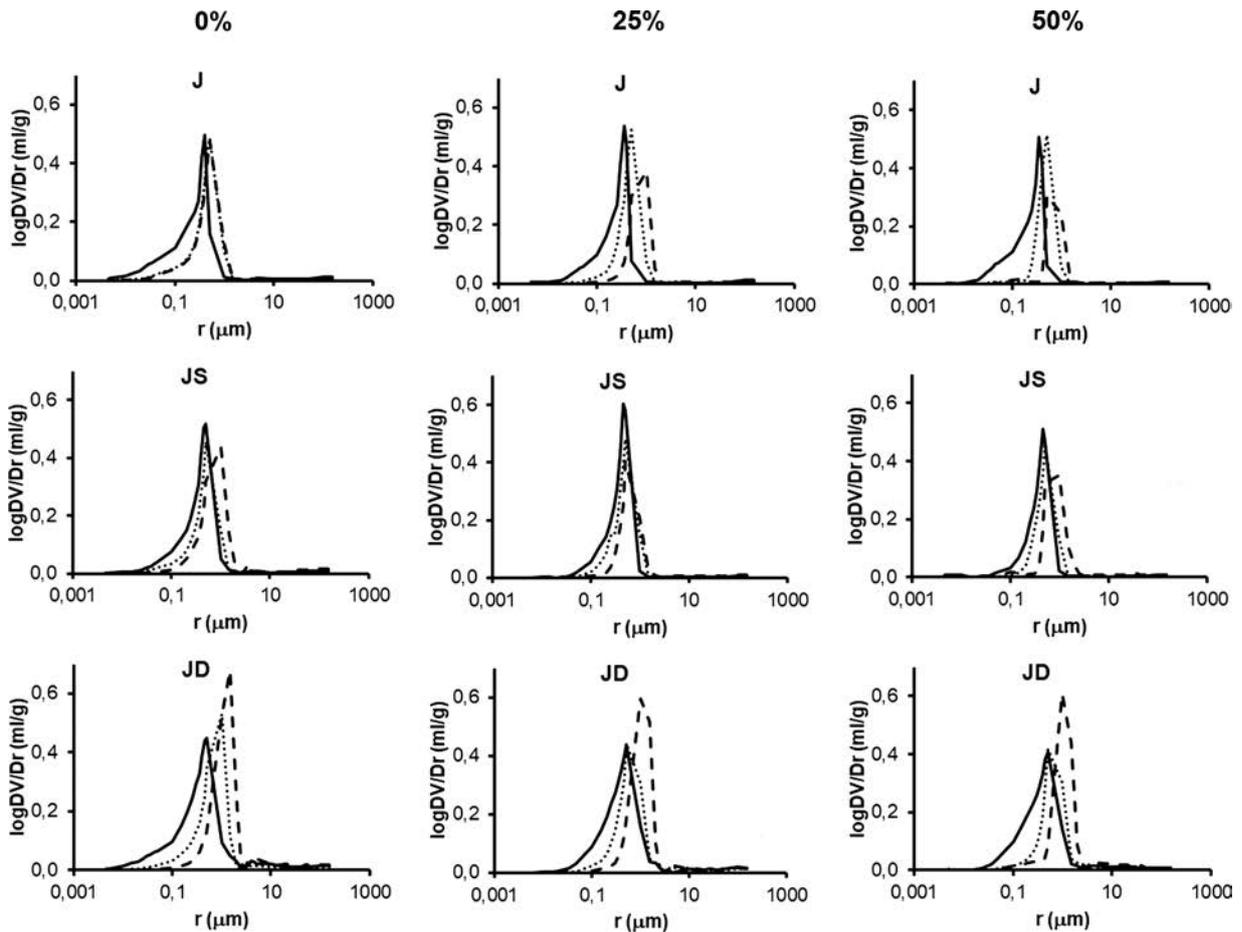


FIGURE 1. Pore size distribution curves for bricks without additives (J), with halite (JS) and with calcined diatomite sludge (JD) fired at 800, 950 and 1100 $^{\circ}\text{C}$, either untreated (no consolidant - 0%) or treated with 25% and 50% concentrations of ethyl silicate. Pore radius (in μm) versus $\log(\text{DV}/\text{Dr})$ (in ml/g). Legend: continuous line = 800 $^{\circ}\text{C}$; dotted line = 950 $^{\circ}\text{C}$; dashed line = 1100 $^{\circ}\text{C}$.

TABLE 1. Results of MIP test on brick samples fired at 800, 950 and 1100 °C, untreated (0%) and treated with 25% and 50% of ethyl silicate. SSA = specific surface area (m²/g); ρ_a = apparent density (g cm⁻³); ρ_r = real density (g cm⁻³); P_o = open porosity (%).

		J800	J950	J1100	JS800	JS950	JS1100	JD800	JD950	JD1100
0%	SSA	5.85	2.27	2.09	2.98	1.77	1.12	5.48	2.10	1.32
	ρ_a	1.49	1.47	1.48	1.45	1.46	1.39	1.29	1.23	1.28
	ρ_r	2.41	2.44	2.51	2.47	2.51	2.45	2.41	2.25	2.31
	P_o	38.32	39.75	40.86	41.42	41.75	43.36	46.43	45.25	44.83
25%	SSA	3.84	1.51	1.02	1.98	1.28	0.92	2.69	1.52	0.77
	ρ_a	1.57	1.53	1.38	1.54	1.51	1.48	1.32	1.35	1.35
	ρ_r	2.53	2.50	2.10	2.49	2.51	2.52	2.38	2.47	2.48
	P_o	37.93	38.76	34.47	38.14	39.63	41.34	44.59	45.51	45.36
50%	SSA	3.75	1.03	1.24	2.80	1.02	0.81	2.63	1.54	1.02
	ρ_a	1.54	1.59	1.60	1.58	1.56	1.49	1.36	1.40	1.37
	ρ_r	2.43	2.41	2.52	2.39	2.55	2.46	2.38	2.45	2.42
	P_o	36.43	34.10	36.57	33.87	38.65	39.19	42.92	42.73	43.47

TABLE 2. Amorphous versus crystal ratio estimation (a/c) determined by X-ray diffraction on brick samples fired at 800, 950 and 1100 °C.

	J800	J950	J1100	JS800	JS950	JS1100	JD800	JD950	JD1100
a/c	0.042	0.069	0.106	0.055	0.068	0.088	0.051	0.064	0.118

unimodal pore size distribution although the commonest size becomes larger as the firing temperature increases. These changes are even more evident if we compare them with bricks without additives. In fact, in the bricks with added halite the maximum peak rose from 0.45 μm at 800 °C to 1 μm at 1100 °C, and when calcined diatomite sludge was used as the additive, the maximum peak on the porometric curve jumped from 0.5 μm at 800 °C to 1.5 μm at 1100 °C (Figure 1). The real density values (ρ_r , Table 1) were as expected for brick, a material rich in quartz and phyllosilicates. The lowest values were measured in the bricks with added 10 wt.% calcined diatomite sludge. This is because this waste is rich in quartz and cristobalite (35, 36) which have lower densities than most other minerals (Ca-plagioclases, muscovite, carbonates and newly formed silicates) that characterize the mineralogy of bricks. As might be expected, the lowest apparent density values (ρ_a , Table 1) were also found in the bricks made with calcined diatomite sludge, which were the most porous.

There are important differences in the porous systems of the bricks treated with ethyl silicate compared to those of untreated bricks. First of all, the open porosity decreases, which indicates that part of the space previously occupied by pores has now been filled by the consolidant. When the amount of consolidant is increased from 25% to 50% of ethyl silicate, the porosity falls even further (P_o , Table 1). However, in general terms the fall in porosity is not

directly related with the type of brick being tested or with the firing temperature of the bricks. This may be due to the fact that the consolidant was applied with a brush and not by immersion or absorption by capillarity, which according to some researchers would have produced a more homogeneous absorption of the product (22, 37), although others disagree (38). In spite of the possible benefits in terms of uniformity of applying the consolidant by immersion, our aim was to test the consolidant in the conditions in which it is normally applied in building restoration and conservation work.

If we compare the different types of bricks more specifically, the treatment with 25% ethyl silicate leads to a fall in the porosity of all the samples, except for JD fired at 950 °C and 1100 °C in which the values hardly changed compared to the untreated samples. When 50% of the product was applied, the porosity of the bricks made with calcined diatomite sludge also fell and now all the bricks have a lower porosity compared to the untreated samples. The precipitation of ethyl silicate in the pore network of bricks leads to a decrease in the number of small pores. This can be deduced by the reduction observed in the Specific Surface Area value (SSA, Table 1). In fact, even if the highest SSA values were still found in the bricks without additives and those with calcined diatomite sludge fired at 800 °C, they are now less than 4 m²/g. SSA values are lower at higher concentrations of ethyl silicate. In two cases the SSA

value even fell below 1 (JD1100 treated with 25% of product and JS1100 with 50% of product, Table 1). The real and apparent densities are not influenced by the proportion of consolidant product applied and a general slight increase in these values can be observed (Table 1). The pore size curves continue to show a unimodal distribution with a maximum radius of around 1 μm . This maximum continues to shift toward higher values in line with the firing temperature, albeit to a lesser degree if we compare it with the untreated samples.

3.2. Compactness

In the velocity of propagation of the ultrasonic waves it is important to take into account the heterogeneity and the anisotropy of the bricks, which depend on the mineralogical composition, degree of vitrification, density and presence of pores/fissures in the material (39). If part of the empty space is going to be occupied by a consolidant, the velocity will inevitably increase (40, 41). The strongly anisotropic nature of the bricks (ΔM , Table 3) is confirmed by the ultrasounds in that the velocities of wave propagation measured perpendicular to the bed, stretcher and header faces of each brick are quite different. This is especially true of the wave velocity measured perpendicular to the bed, which is always the lowest. This happens because the laminar minerals (above all the phyllosilicates) are orientated in line with this surface due to the pressure applied to the clayey mass during the molding process. The ultrasounds therefore take longer to travel through them. As the firing temperature increases, ΔM tends to fall (the pieces become more homogeneous) due to increased vitrification of the bricks and a gradual loss of the laminar habit of the phyllosilicates (dehydroxilation of these crystals and development of a cellular texture; 42). The highest velocities were measured in the bricks without additives and in general the velocity increased in line with the firing temperature

above all at 1100 °C (Table 3). The increase in velocity is also indicative of greater vitrification of the bricks (Table 2) (26, 43). Of particular note is the high velocity measured in the bricks made with halite fired at 800 °C. This is due as mentioned earlier to the fact that this salt acts as a melting agent. When the samples are treated with the consolidant, the velocity always increases, normally in line with an increase in the firing temperature and is greater when the concentration of the product is increased from 25% to 50% (ΔV_p , Table 3). This increase is higher in the bricks made with halite and with calcined diatomite sludge. Indeed, the bricks with additives were more porous than those without (Table 1) and this may have resulted in deeper penetration of the ethyl silicate.

3.3. Color

Spectrophotometry plays an important role in the field of architectural heritage conservation. In the specific case of the application of a consolidant product to protect bricks or other building materials, a colorimetric study of its effects can quantify the degree to which the chromaticity and lightness of the material has changed, and whether this change is aesthetically significant. The untreated bricks have orangey colors except for those in which halite was used as an additive, which have a yellowish tone. Rye (44) observed that the addition of this salt to a clayey earth changed the color of the fired bricks, making them yellower. All the pieces fired at 1100 °C were darker. This is confirmed by the decrease in the a^* and/or L^* values (Table 4). The application of ethyl silicate at both 25% and 50% causes a reduction in L^* while the chromaticity values a^* and b^* rise. Indeed, saturation normally increases compared to the values for the untreated samples (C, Table 4). In order to evaluate how the application of ethyl silicate has influenced these materials, we measured the color difference (ΔE),

TABLE 3. Mean values of ultrasonic wave velocities (in m/s) for untreated bricks (0%) and for bricks treated with 25% and 50% concentrations of ethyl silicate. The structural anisotropy (ΔM , in %) of each brick is indicated in brackets. ΔV_p stands for the increase in velocity (in %) after treatment with the consolidant.

	0%	25%	$\Delta V_{p(25\%)}$	50%	$\Delta V_{p(50\%)}$
J800	1942 (60.32)	1952 (64.36)	0.51	1978 (61.67)	1.85
J950	1944 (60.36)	2045 (63.65)	5.20	2010 (62.31)	3.40
J1100	2147 (58.27)	2165 (60.71)	0.84	2364 (61.37)	10.11
JS800	1844 (62.25)	1901 (60.14)	3.09	1914 (55.42)	3.80
JS950	1687 (60.02)	1825 (59.41)	8.18	1912 (62.57)	13.34
JS1100	1744 (55.68)	2028 (59.51)	16.28	2021 (57.28)	15.88
JD800	1700 (53.63)	1734 (59.23)	2.00	1814 (58.95)	6.71
JD950	1712 (61.60)	1728 (60.59)	0.93	1867 (58.19)	9.05
JD1100	1906 (57.22)	2073 (55.17)	8.76	2204 (58.62)	15.63

TABLE 4. Lightness (L^*), chromatic coordinates (a^* and b^*), chroma (C^*), hue angle (H°) and color difference (ΔE) values for untreated bricks (0%) and for bricks treated with 25% and 50% concentrations of ethyl silicate.

		J800	J950	J1100	JS800	JS950	JS1100	JD800	JD950	JD1100
0%	L^*	56.58	62.30	57.37	67.00	72.58	64.05	60.66	64.91	56.29
	a^*	15.96	15.95	10.47	11.26	7.96	7.59	13.70	14.71	10.91
	b^*	18.36	20.30	20.19	18.43	18.21	24.51	16.99	20.30	20.06
	C^*	24.33	25.82	22.74	21.60	19.87	25.66	21.83	25.07	22.84
	H°	49.00	51.84	62.60	58.58	66.38	72.80	51.13	54.08	61.47
25%	L^*	54.60	55.22	56.63	68.07	69.36	50.57	60.96	58.96	58.70
	a^*	15.54	18.78	11.05	10.65	8.62	9.80	15.36	16.89	9.64
	b^*	18.22	23.01	20.53	18.6	18.35	18.02	19.61	21.93	20.62
	C^*	23.95	29.70	23.31	21.48	20.27	20.51	24.91	27.68	22.76
	H°	49.53	50.78	61.70	60.29	64.84	61.45	51.92	52.39	64.93
	ΔE	2.03	5.89	0.30	0.84	3.14	11.60	3.08	5.29	1.97
50%	L^*	54.38	53.95	57.08	66.51	73.46	54.50	61.50	63.30	54.95
	a^*	18.32	20.60	11.82	11.23	7.04	10.56	14.46	15.21	9.60
	b^*	21.27	24.61	20.87	18.66	20.23	20.69	18.00	20.37	19.19
	C^*	28.07	32.09	23.98	21.78	21.42	23.23	23.09	25.42	21.46
	H°	49.27	50.07	60.48	58.96	70.80	62.96	51.22	53.24	63.41
	ΔE	2.95	5.43	1.48	0.43	2.03	8.23	0.94	1.52	0.82

taking the untreated samples as a reference. ΔE was almost always less than 5, the threshold above which the change in color can be appreciated by the human eye (45). In just a few cases, J950 treated at 25% and 50%, JD950 treated at 25% and above all, JS1100 treated at 25% and 50%, the threshold of 5 was exceeded (Table 4). The application of the product at a concentration of 50% did not result in greater color differences compared to that at 25%. In fact, in most of the cases the ΔE for the samples treated with 50% ethyl silicate was lower than that for the samples treated at 25% concentration.

3.4. Durability

The decay suffered by a material depends among other factors on its porous system (46). This means that one way of evaluating the durability of a brick whose porosity and compactness have been altered by the application of a consolidant is by assessing the damage produced by the soluble salts that crystallize inside it. Using the salt crystallization test we were able to assess, even visually the consolidant capacity of the product. In all the untreated bricks we observed an increase in weight after the first test cycle due to the absorption and crystallization of the salts in the pores of the samples. This increase was greater in J800 and JD800 (Figure 2), the bricks with the highest SSA value (SSA, Table 1). The other samples absorbed less salts, especially the three samples fired at the highest temperature, which were

probably the most vitrified. As the number of test cycles increased, the bricks continued to increase in weight, although to a lesser degree than at the beginning and there were slight oscillations as a result of the loss of material due to the disintegrating effects of the sodium sulfate (Figure 2). With the naked eye, we observed that the loss of material began at the edges of the test samples, the areas most vulnerable to attack by the salts (47). There was a small drop in weight in samples JS1100 and JD1100 between cycles 6 and 7 due to the loss of some fragments, but it remained unchanged thereafter. The drop in weight of J800 in cycles 9 and 10 was more pronounced, which indicates severe material loss. This brick was somewhat exceptional, in that it was the only brick that underwent a considerable increase in weight until cycle 7. This implies that it must have had a high concentration of salt inside it. By contrast, as early as the third cycle onwards JD800 showed a slight, but constant loss in weight, indicating a gradual crumbling of the material. The other brick fired at 800 °C, JS800, has a similar durability to the bricks fired at 950 °C due to the greater vitrification of these bricks produced by the melting agent capacity of the halite. Although JS950 absorbs more salt in the first two test cycles, it follows a similar curve to the bricks fired at 1100 °C.

The application of the ethyl silicate leads to some improvements in the resistance of the bricks to attack by salts (Figure 2). J800 and JD800 were still the bricks that most increased in weight after the first

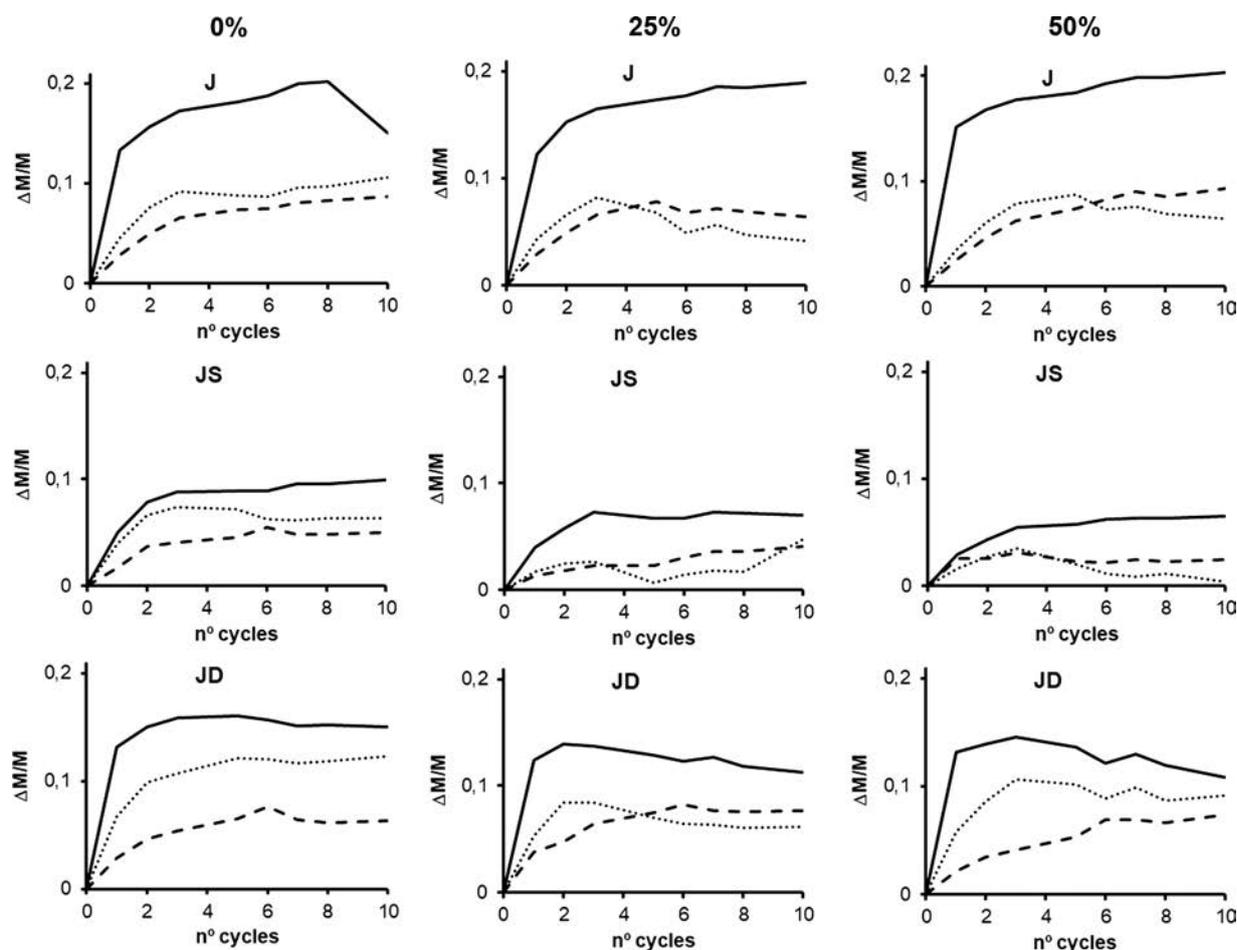


FIGURE 2. Weight variation ($\Delta M/M$, in %) in untreated bricks (0%) and in bricks treated with 25% and 50% concentrations of ethyl silicate subjected to the salt crystallization test. Legend: continuous line = 800 °C; dotted line = 950 °C; dashed line = 1100 °C.

test cycle. However, J800 managed to get through all 10 cycles without breaking, while the loss in weight in JD800 did not happen gradually as in the untreated samples, and instead took place in sudden leaps, which were more accentuated the higher the concentration of the consolidant. While the untreated samples suffered superficial crumbling, these samples suffered the loss of thicker fragments due to the increased cohesion between the grains achieved by the consolidant. The decay produced by the salt crystallization test was particularly clear in JD950 treated with 50% ethyl silicate. In this brick we observed an increase in weight of almost 11% up until cycle 3 of the test, due to the penetration of the salt inside the bricks. Between cycles 5 and 6 however, the salts exert pressure on the bricks and creating new pores and fissures. This led to flaking on the surface and the weight of the brick began to fall. Later, in cycle 7, the weight of the brick increased again as more salts began to crystallize in the new empty spaces that had been created. These salts would later be responsible for a subsequent loss of weight and material

in cycle 8. J950 treated with 25% and 50% ethyl silicate went through a similar process. The samples with the smallest weight increase were those made with added halite and fired at 950 °C and 1100 °C (Figure 2), especially JS1100 which showed minimal oscillations in the curves implying that very little material was lost.

In order to indirectly assess the degree of decay reached by the bricks, we measured the ultrasound propagation velocity during different phases of the salt crystallization test. This provided more information about the decay of the bricks treated with ethyl silicate and a more reliable interpretation of the results. The first measurement of the ultrasound waves was carried out before starting the accelerated ageing test and before treating the samples with the ethyl silicate. In the two diagrams in Figure 3 this is point 0 on the horizontal axis. We then measured the velocity of the ultrasounds after applying the treatments. Point 1 on the diagrams indicates the measurement on treated samples that were not subjected to the ageing test. Finally, we made two

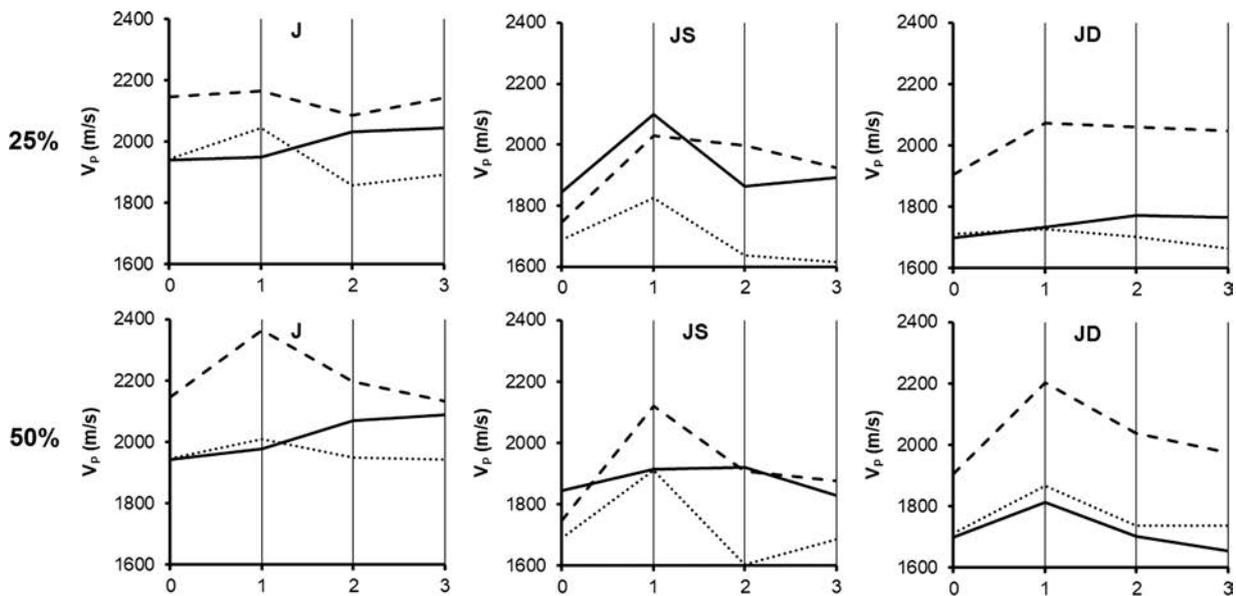


FIGURE 3. Ultrasound measurements (V_p , in m/s) performed on bricks without and with additives fired at 800, 950 and 1100 °C. The horizontal axis shows the measurements taken at the following stages: 0 = untreated bricks; 1 = bricks treated with 25% and 50% concentrations of ethyl silicate; 2 = after 5 salt crystallization cycles; 3 = at the end of the accelerated ageing test. Legend: continuous line = 800 °C; dotted line = 950 °C; dashed line = 1100 °C.

further measurements in cycles 5 and 10 of the test, which are represented on the diagrams as points 2 and 3 respectively. It is clear that the application of the ethyl silicate at concentrations of 25% and 50% always results in an increase in velocity, due to the polymerization of the product in the pores of the bricks (point 1 of the two diagrams in Figure 3). The increase in velocity is normally more accentuated with higher concentrations of the product. The ultrasound measurements in cycles 5 and 10 of the ageing test highlight the fact that many bricks are attacked by salts, even though the damage was not visible to the naked eye and the change in weight in Figure 2 could not be clearly detected in all of them. Indeed, after five cycles of the accelerated ageing test (point 2) at least three types of bricks treated with 25% ethyl silicate (J950, JS800 and JS950) and six samples treated with 50% (J1100, JS950, JS1100, JD800, JD950 and JD1100) underwent a significant fall in velocity. This suggests that fissures had developed inside the brick due to the process of dissolution and crystallization of the sodium sulfate. It is important to note for example that these samples include those made with halite (JS), which had undergone very few changes in weight and a priori seemed to be healthier, especially those fired at 950 and 1100 °C. This means that although to the naked eye the samples appear to be intact, they have in fact begun to decay. This decay process continues until the end of the test (point 3): the velocity continues to fall in some samples because the fissuring increases even more, while in others the velocity

increases again because new salt begins to crystallize in the pores. In general, the variations in the velocity of the ultrasounds are less pronounced when the consolidant is applied in more diluted form, in other words when we use a 25% concentration of ethyl silicate. This result seems to indicate that the most diluted treatment managed to penetrate more deeply and that this amount of consolidant was sufficient to improve the degree of cohesion in most of the bricks. By contrast the treatment with a 50% concentration developed a more compact structure but without penetrating deeply. Once the salt had attacked and broken off the more compact outer layer, as happened in sample JD950 described above, the bricks were left unprotected against new salt attacks.

4. CONCLUSIONS

We assessed the efficacy of the ethyl silicate as a consolidant of solid bricks with different compositions (without additives and with added halite or calcined diatomite sludge) fired at three different temperatures (800, 950 and 1100 °C). For this purpose, we chose two different concentrations of the consolidant (25% and 50%) diluted in white spirit. Our study of the porous system of the bricks revealed that once the consolidant had been applied and had polymerized, it reduced the open porosity, although this reduction was not very significant when a 25% concentration of ethyl silicate was used and the pore size was almost unaffected by

either treatment. The number of small pores fell considerably (in some cases the specific surface area fell by as much as 50%). This is a positive change given that these pores can have a negative effect on the durability of the brick. The increase in velocity recorded in the ultrasound test shows that both treatments increase the compactness of the bricks, which was almost always higher in the bricks treated with a higher concentration of product. In terms of color, the ethyl silicate did not bring about important modifications in the lightness and chromaticity of the pieces with the exception of the bricks made with halite and fired at 1100 °C, which underwent changes that were visible to the human eye. A higher concentration of the product does not necessarily lead to a more pronounced change in the color of the bricks. The improvement in the physical behavior of the bricks could also be noted after the accelerated ageing test in which although the consolidated bricks did suffer decay due to attack by the salts, they were more durable than the untreated bricks. However, the consolidant was not equally effective in all samples and resistance to decay does not improve when the concentration of the product is increased, as might have been expected after the results obtained for pore size and ultrasounds. In general, the best durability results were achieved when the treatment was applied with a concentration of 25%. Our findings suggest that at this concentration the product managed to penetrate more deeply and improve the cohesion between the mineral grains in the bricks. The treatment with 50% ethyl silicate did not penetrate very deeply and created a surface layer that was rich in silica but suffered flaking after attack by the salts. This research shows the need for complementary techniques to be used to contrast the results obtained, assess their reliability and rule out possible erroneous conclusions. The combination of the ultrasound test and the accelerated ageing test revealed something which would otherwise have been invisible, i.e. the decay that some of the apparently healthy bricks were undergoing. Future research should also consider brick resistance to microdrilling and texture observation under SEM in order to measure the penetration depth of ethyl silicate in brick samples and to provide a more complete picture of their consolidation.

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REFERENCES

1. Winkler, E. M. (1973) *Stone: properties, durability in man's environment*. Springer, New York. <https://doi.org/10.1007/978-3-7091-4120-5>
2. Alves, C.; Sanjurjo Sánchez, J. (2015) Maintenance and Conservation of Materials in the Built Environment. In: *Pollutants in Buildings, Water and Living Organisms* (Lichtfouse E., Schwarzbauer J., Robert D. eds.). Springer, Cham, pp. 1–50. https://doi.org/10.1007/978-3-319-19276-5_1
3. Lazzarini, L.; Laurenzi Tabasso, M. (1986) *Il restauro della pietra*. CEDAM, Padova.
4. Snethlage, R. (2014) Stone Conservation. In: *Stone in architecture. Properties, durability* (Siegesmund, S. and Snethlage, R. eds.). Springer, Berlin, pp. 415–550. https://doi.org/10.1007/978-3-642-45155-3_7
5. Sierra Fernandez, A.; Gomez Villalba, L. S.; Rabanal, E. M. E.; Fort, R. (2017) New nanomaterials for application and restoration of stony materials: a review. *Mater. Construcc.* 67, e107. <https://doi.org/10.3989/mc.2017.07616>
6. Esbert, R. M.; Grossi, C.; Marcos, R. M. (1987) Estudios experimentales sobre la consolidación y protección de los materiales calcáreos de la Catedral de Oviedo. 1ª parte. *Mater. Construcc.* 37, 17–25. <https://doi.org/10.3989/mc.1987.v37.i206.867>
7. Esbert, R. M.; Díaz Pache, F. (1993) Influencia de las características petrofísicas en la penetración de consolidantes en rocas monumentales porosas. *Mater. Construcc.* 43, 25–36. <https://doi.org/10.3989/mc.1993.v43.i230.681>
8. Cultrone, G.; Madkour, F. (2013) Evaluation of the effectiveness of treatment products in improving the quality of ceramics used in new and historical buildings. *J. Cult. Herit.* 14, 304–310. <https://doi.org/10.1016/j.culher.2012.08.001>
9. Marques, M. L.; Chastre, C. (2014) Effect of consolidation treatments on mechanical behaviour of sandstone. *Constr. Build. Mater.* 70, 473–482. <https://doi.org/10.1016/j.conbuildmat.2014.08.005>
10. Cnudde, V.; Dierick, M.; Masschaele, B.; Jacobs P. J. (2006) A high resolution view at water repellents and consolidants: critical review and recent developments. In: *fracture and failure of natural building stones* (Kourkoulis, S. K. ed.), Springer, Dordrecht, pp. 519–540. https://doi.org/10.1007/978-1-4020-5077-0_32
11. Warren, J. (1999) *Conservation of brick*. Butterworth Heinemann, Oxford, UK.
12. Manning, D. A. C. (1995) *Introduction to industrial minerals*. Chapman & Hall, London, UK. <https://doi.org/10.1007/978-94-011-1242-0>
13. Cultrone, G.; Sebastián, E.; Elert, K.; Torre, M. J. de la; Cazalla, O.; Rodríguez Navarro, C. (2004) Influence of mineralogy and firing temperature on porosity of bricks. *J. Eur. Ceram. Soc.* 24, 547–564. [https://doi.org/10.1016/S0955-2219\(03\)00249-8](https://doi.org/10.1016/S0955-2219(03)00249-8)
14. Muñoz Velasco, P.; Morales Ortiz, M.P.; Mendivil Giró, M.A.; Muñoz Velasco, L. (2014) Fired clay bricks manufactured by adding wastes as sustainable construction material. A review. *Constr. Build. Mater.* 63, 97–107. <https://doi.org/10.1016/j.conbuildmat.2014.03.045>
15. Cultrone, G.; Rodríguez Navarro, C.; Sebastián, E.; Cazalla, O.; Torre, M. J. de la (2001) Carbonate and silicate phase reactions during ceramic firing. *Eur. J. Mineral.* 13, 621–634. <https://doi.org/10.1127/0935-1221/2001/0013-0621>
16. Grapes, R. (2006) *Pyrometamorphism*. Springer, Berlin, Germany.
17. Liu, R.; Han, X.; Huang, X.; Li, W.; Luo, H. (2013) Preparation of three component TEOS-based composites for stone conservation by sol-gel process. *J Sol-Gel Sci. Technol.* 68, 19–30. <https://doi.org/10.1007/s10971-013-3129-z>
18. Villegas Sánchez, R.; Baglioni, R.; Sameño Puerto, M. (2003) Tipología de materiales para tratamiento. In: *Cuadernos Técnicos vol. 8: Metodología de diagnóstico y evaluación de tratamientos para la conservación de los edificios históricos* (Villegas Sánchez R. y Sebastián Pardo E., eds.), Comares, Granada, Spain, pp. 168–193.

19. Scherer, G. W.; Wheeler, G. S. (2009) Silicate consolidants for stone. *Key Eng. Mater.* 391, 1–25. <https://doi.org/10.4028/www.scientific.net/KEM.391.1>
20. Franzoni, E.; Graziani, G.; Sassoni, E. (2015) TEOS-based treatments for stone consolidation: acceleration of hydrolysis-condensation reactions by poulticing. *J. Sol-Gel Sci. Technol.* 74, 398–405. <https://doi.org/10.1007/s10971-014-3610-3>
21. Franzoni, E.; Pigino B.; Leemann, A.; Lura P. (2014) Use of TEOS for fired-clay bricks consolidation. *Mater. Struct.* 47, 1175–1184. <https://doi.org/10.1617/s11527-013-0120-7>
22. Franzoni, E.; Graziani, G.; Sassoni, E.; Bacilieri, G.; Griffa, M.; Lura, P. (2015) Solvent-based ethyl silicate for stone consolidation: influence of the application technique on penetration deep, efficacy and pore occlusion. *Mater. Struct.* 48, 3503–3515. <https://doi.org/10.1617/s11527-014-0417-1>
23. Torraca, G. (2009) Lectures on materials science for architectural conservation. The Getty Conservation Institute, Los Angeles, USA.
24. Elert, K.; Sebastián Pardo, E.; Rodríguez Navarro, C. (2015) Alkaline activation as an alternative method for the consolidation of earthen architecture. *J. Cult. Herit.* 16, 461–469. <https://doi.org/10.1016/j.culher.2014.09.012>
25. Bermúdez Sánchez, C.; Rueda Quero, L.; Cultrone, G. (2012) Caracterización de los yacimientos de arcilla en la provincial de Granada aplicada al conocimiento de los bienes de interés histórico-artístico. Proceedings of the I International Congress “El Patrimonio Natural como Motor de Desarrollo: Investigación e Innovación” (Peinado Herrerros M. A. ed.), 728–740.
26. De Rosa, B.; Cultrone, G. (2014) Assessment of two clayey materials from northwest Sardinia (Alghero district, Italy) with a view to their extraction and use in traditional brick production. *Appl. Clay Sci.* 88–89, 100–110. <https://doi.org/10.1016/j.clay.2013.11.030>
27. Martin, J. D. (2016) X Powder, X Powder12, X PowderXTM. A software package for powder X-ray diffraction analysis, Lgl. Dp. GR-780–2016.
28. ASTM D2845. (2005) Standard test method for laboratory determination of pulse velocities and ultrasonic elastic constant of rock, USA.
29. Guydader, J.; Denis, A. (1986) Propagation des ondes dans les roches anisotropies sous contrainte évaluation de la qualité des schistes ardoisiers. *Bull. Eng. Geol.* 33 49–55. <https://doi.org/10.1007/BF02594705>
30. EN 15886. (2011) Conservation of cultural property. Test methods. Colour measurement of surfaces, AENOR, Madrid.
31. EN 12370. (2001) Metodi di prova per pietre naturali. Determinazione della resistenza alla cristallizzazione dei sali. CNR-ICR, Rome, Italy.
32. Espinosa Marzal, R.M.; Hamilton, A.; McNall, M.; Whitaker, K.; Scherer, G.W. (2011) The chemomechanics of crystallization during rewetting of limestone impregnated with sodium sulfate. *J. Mater. Res.* 26, 1472–1481. <https://doi.org/10.1557/jmr.2011.137>
33. Martínez, P.; Soto, M.; Zunino, F.; Stuckrath, C.; Lopez, M. (2016) Effectiveness of tetra-ethyl-ortho-silicate (TEOS) consolidation of fired-clay bricks manufactured with different calcination temperatures. *Constr. Build. Mater.* 106, 209–217. <https://doi.org/10.1016/j.conbuildmat.2015.12.116>
34. Kingery, W. D. (1960) Introduction to ceramics. John Wiley & Sons, Inc., New York.
35. Ediz, N.; Bentli, I.; Tatar, I. (2010) Improvement in filtration characteristics of diatomite by calcination. *Int. J. Miner. Process.* 94, 129–134. <https://doi.org/10.1016/j.minpro.2010.02.004>
36. Ferraz, E.; Coroado, J.; Silva, J.; Gomes, C.; Rocha, F. (2011) Manufacture of ceramic bricks using recycled Brewing spent kieselguhr. *Mater. Manuf. Processes* 26, 1319–1329. <https://doi.org/10.1080/10426914.2011.551908>
37. Ferreira Pinto, A. P.; Delgado Rodrigues, J. (2008) Stone consolidation: the role of treatment procedures. *J. Cult. Herit.* 9, 38–53. <https://doi.org/10.1016/j.culher.2007.06.004>
38. Costa, D.; Leal, A. S.; Mimoso, J. M.; Pereira, S. M. R. (2017) Consolidation treatments applied to ceramic tiles: are they homogeneous? *Mater. Construcc.* 67, e113. <https://doi.org/10.3989/mc.2017.09015>
39. Bourret, J.; Tesser Doyen, N.; Guinebretiere, R.; Joussein, E.; Smith, D.S. (2015) Anisotropy of thermal conductivity and elastic properties of extruded clay-based materials: evolution with thermal treatment. *Appl. Clay Sci.* 116–117, 150–157. <https://doi.org/10.1016/j.clay.2015.08.006>
40. Ferreira Pinto, A. P.; Delgado Rodrigues, J. (2012) Consolidation of carbonate stones: influence of treatment procedures on the strengthening of consolidants. *J. Cult. Herit.* 13, 154–166. <https://doi.org/10.1016/j.culher.2011.07.003>
41. Esbert, R. M.; Ordaz, J.; Alonso, F. J.; Montoto, M. (1997) Manual de diagnosis y tratamiento de materiales pétreos y cerámicos. Col.legi d’Aparelladors i Arquitectes Tècnics de Barcelona.
42. Rodríguez Navarro, C.; Cultrone, G.; Sanchez Navas, A.; Sebastián, E. (2003) TEM study of mullite growth after muscovite breakdown. *Am. Mineral.* 88, 713–724. <https://doi.org/10.2138/am-2003-5-601>
43. Papargyris, A.D.; Cooke, R.G.; Papargyri, S.A.; Botis, A.I. (2001) The acoustic behavior of bricks in relation to their mechanical behavior. *Constr. Build. Mater.* 15, 361–369. [https://doi.org/10.1016/S0950-0618\(01\)00007-1](https://doi.org/10.1016/S0950-0618(01)00007-1)
44. Rye, O.S. (1976) Keeping your temper under control: materials and manufacture of Papuan pottery. *Archeol. Phys. Anthropol. Oceania* 11, 106–137.
45. Grossi, C.M.; Brimblecombe, P.; Esbert, R.M.; Alonso, F.J. (2007) Color changes in architectural limestones from pollution and cleaning. *Color Res. Appl.* 32, 320–331. <https://doi.org/10.1002/col.20322>
46. Dohene, E.; Price, C.A. (2010) Stone conservation. An overview of current research. The Getty Conservation Institute, Los Angeles, USA.
47. Inkpen, R. J.; Petley, D.; Murphy, W. (2004) Durability and rock properties. In: Stone decay. Its causes and controls (Smith B. J. and Turkington A. V. eds.). Donhead Publishing Ltd., Routledge, Abingdon, UK.