Consolidation of fired-clay bricks by ethyl silicate: durability to salt crystallization

E. Franzoni*, E. Sassoni, G. Graziani and A. Fregni
Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Bologna, Italy
* elisa.franzoni@unibo.it

Abstract

The resistance of ethyl silicate-consolidated bricks to sodium sulfate crystallization cycles was evaluated. A commercial ethyl silicate (ES) based product was applied by brushing with 5 or 10 strokes to assess the effect on distribution/accumulation of the consolidant inside the pores. After long-term curing, aimed at making ES-treated samples lose their temporary hydrophobicity, samples were characterized by assessing the penetration depth of consolidants, tensile strength and modifications in open porosity and pore size distribution. Resistance to salt crystallization was evaluated by carrying out sodium sulfate crystallization cycles. The capillary suction of the salt solution was let occur through the untreated surface of cubic samples treated in the upper face, in order to investigate brick response to salts coming from behind the consolidated layer (the situation usually occurring when rising damp is present). Treatment with either 5 or 10 strokes provided protection against salt damage, and no accumulation of salt behind the consolidated layer was observed.

Keywords: terracotta, ethyl silicate, rising damp, sodium sulfate, bricks

1   Introduction

The need of finding suitable materials for consolidation of fired-clay elements in ancient buildings, such as bricks and terracotta decorative parts, is an urgent task, as they are widely diffused in historical architecture and severely affected by weathering phenomena, causing disaggregation, flaking and detachments [1]. Despite this urgency, however, the study of this topic is not as intensive as might be expected [1].

Recently, the effects of brick consolidation by ethyl silicate (ES), which is the most widely used consolidant for natural stone [2, 3], has been investigated [1]. ES was chosen because it exhibits good effectiveness when OH^- groups are present on the pore surface of materials, allowing chemical bonding with silica gel that forms due to curing reactions [3]. As bricks contain relevant silicate fractions, some chemical adhesion between material and consolidant is expected and indeed encouraging preliminary results have been obtained [1].

However, several aspects still need to be fully investigated about the use of ethyl silicate for brick consolidation, such as the effects of different treating procedures and the treatment durability. Indeed, the application procedure is a key factor in determining the effects of a consolidation treatment, as it controls the consolidant penetration depth and product uptake and hence the final performances [4, 5].

With regard to durability, the behaviour of brick consolidated by ethyl silicate has not been fully elucidated yet. This topic seems to be particularly relevant, especially when referring to brick behaviour towards salt weathering, since conservation works are often carried out without removing completely (or even without removing at all) rising damp, and salt crystallisation may continue after the intervention [6]. If variations in the substrate properties induced by the consolidant are not carefully considered, the degradation processes could even be aggravated by the intervention. On this topic, different opinions can be found in the literature about the effects of ethyl silicate. According to some authors, ES should increase resistance to salt crystallization, by increasing samples tensile strength [2]. However, depending on the support, ethyl silicate treatment might increase the fraction of smaller pores, hence increasing material susceptibility to salt damage [7].

In this paper the resistance to salt crystallization of brick consolidated with ethyl silicate was investigated. Two different application procedures (involving a different number of brushing strokes) were followed and their effects were compared, in terms of efficacy and compatibility. The two application procedures involve brushing, as it is the easiest and hence the most used on site [4, 8]. Even though technical data sheets of commercial products usually recommend brushing until apparent refusal, a much lower number of applications is normally performed in the field. Therefore, two treatment procedures were tested: an application number closer to

apparent refusal (10 strokes) and one closer to the common on-site practice (5 strokes).

The behaviour of the treated samples towards salt weathering was taken into consideration, by evaluating the microstructure alteration and salt content of samples subjected to crystallization cycles of a 14 wt.% sodium sulphate solution. Particular attention was devoted to the behaviour of the treated layer with respect to the underlying one, in order to determine whether the consolidated part would allow the salts to exit the samples, or whether it would act as a clogging layer, possibly resulting in the detachment of the treated portion of the samples.

2   Materials and methods

2.1   Bricks

Commercial fired-clay bricks (25 × 12 × 5.5 cm^3, RDB, Pontenure, Italy) were cut into 4 × 4 × 4 cm^3 cubes and cylinders with 2 cm diameter and 5 cm height. All the samples of the same shape were taken from the same brick, so that the obtained results could be unaffected by heterogeneities in the starting materials.

2.2   Ethyl silicate treatments

The ethyl silicate consolidant was applied by 5 brush strokes (samples "T5") and by 10 brush strokes (samples "T10").

A commercial product, composed of 75 wt.% ethyl silicate (including 1% dibutyltin dilaurate as catalyst) and 25 wt.% white spirit (ESTEL 1000 by CTS s.r.l., Italy) was used.

Cylinders were treated on the whole external surface, while cubes were treated on one face only. All treated samples were left curing for 1 month prior to mechanical and microstructural testing, as suggested by the consolidant technical data sheets. Samples to be subjected to salt crystallization cycles were cured for 1 year, to avoid possible surface hydrophobicity owing to incomplete ES hydrolysis-condensation, reportedly lasting as much as 6-7 months [3].

2.3   Characterization techniques

Treatment efficacy was determined in terms of weight gain after treatment, penetration depth and tensile strength, determined on both untreated and treated samples.

Weight gain was measured by weighing cylindrical samples before treatment and after 1 month curing. It was also evaluated whether the higher number of brush strokes of treatment "T10" had resulted in a higher product uptake. Penetration depth was measured after 72 hours curing, as

it might increase in the first hours after treatment, due to some redistribution of the consolidant [9]. Penetration depth was visually assessed by fracturing treated samples and wetting them to highlight the consolidated part (hydrophobic). Indeed, after ES treatment, samples remain temporary hydrophobic until consolidant ethoxy groups fully react [10]. Tensile strength was determined on brick cylinders by the tensile splitting test (loading rate 4 mm/min).

The compatibility of the treatment was evaluated in terms of alterations in sample microstructure, by mercury intrusion porosimetry (MIP), using a Porosimeter 2000 Carlo Erba with a Fisons Macropore Unit 120. MIP was performed on samples obtained by chisel from cylinders used for tensile strength measurement. As increases in the fractions of smaller pores are known to increase a material's susceptibility to salts decay, the percentages of pores in the following ranges were calculated: radius r > 1 µm, 1-0.1 µm, 0.1-0.01 µm, <0.01 µm. Particular attention was devoted to possible increases in the latter two ranges.

After evaluation of treatment efficacy and compatibility, samples were subjected to 5 salt crystallization cycles, performed as described below. Cubic samples treated on one face only were oven dried and then immersed for about 0.5 cm in a 14 wt.% solution of sodium sulphate in deionized water, and kept immersed for 7 hours. Samples were placed in the containers with the treated face up, so that the saline solution would penetrate from the untreated area of the samples and the ability of the consolidated layer to let salts exit from the samples could be evaluated. Immersion was followed by a drying phase, where samples were oven-dried for 15 hours at 50 °C, the temperature being chosen not to damage the consolidant. Finally, samples were left cooling for 2 hours prior to the next cycle.

The effect of salt crystallization cycles was determined by evaluating the weight variation at each cycle, the salt content of treated and untreated samples and the sample total open porosity at the end of the cycles.

Salt content of the samples was determined by ion chromatography (IC), using a Dionex ICS 1000. IC was performed on fragments obtained by chisel from a depth comprised between 0 and 8 mm from the treated face (labelled as "-top"), corresponding to the depth of the consolidated layer, and from a depth comprised between 20 and 40 mm (labelled as "-bottom"), corresponding to the part not reached by the consolidant. Samples were taken at the same depths also in untreated references, for comparison. The salt contents in the consolidated and non-consolidated layers were compared to determine whether the treated layer tends to act as a weir against salt transport. All the upper samples were obtained by excluding efflorescence formed on sample surface. Salt content is reported only in terms of sulphate percentage, as the amount of other salts was found to be negligible.

Sample microstructure was investigated by MIP, performed on samples obtained by chisel from the upper layer of cubes (0-8 mm from the treated surface), near the sample edge, where salt damage was expected to be maximal. To evaluate the opening of micro-cracks due to salt decay, salts were removed from the samples before MIP, by boiling chisel-fractured samples for 30 minutes in deionized water. The efficacy of this procedure in removing salts from brick samples was verified by ion chromatography in preliminary tests (not reported here for brevity's sake).

3   Results and discussion

Physical, mechanical and microstructural properties of treated and untreated samples are reported in Table 1. Both treatments resulted in a remarkable weight increase 1 month after the consolidant application, suggesting that ethyl silicate was retained in pores. T10, as expected, resulted in a higher weight increase compared to T5, consistent with the higher number of brush strokes applied. Consistent with the higher weight increase, treatment T10 reached a higher penetration depth compared to T5 (Table 1), suggesting that the additional amount of consolidant did not form a surface-clogging layer. In both cases, the penetration depth of the consolidant can be considered as satisfactory, also considering that the bricks used for the experiments were highly porous, but they were not subjected to artificial decay prior to the consolidant application.

Tensile strength was found to increase significantly after both treatments, but T10-treated samples exhibited a higher mechanical improvement than T5-treated samples, consistent with their higher consolidant absorption.

Open porosity and pore size distribution of untreated and treated samples are reported in Table 2. Both treatments resulted in some pore occlusion, more marked in the case of T10; however, these alterations are rather limited, hence both treatments can be considered as fairly compatible with bricks in terms of pore occlusion. Regarding pore size distribution, both T5 and T10 led to an increase in the amount of pores in the finest ranges (radius $r < 0.01$ μm and $r < 0.1$ μm), hence some increase in sample susceptibility to salts might be expected, especially in the case of T10, where the increase is more significant. To ascertain whether this is actually the case, salt crystallization cycles were carried out.

Table 1: Weight gain, penetration depth and strength of treated samples (T5 and T10) compared to untreated references (UT)

	Weight gain after 1 month curing [g/cm^2]	Penetration depth [mm]	Tensile strength [MPa]
UT	-	-	3.3
T5	0.02	8	4.3
T10	0.07	11	4.8

Table 2: Total open porosity (OP) and share of the porosity in the indicated pore ranges, for untreated (UT) and treated samples (T5 and T10)

	OP [%]	Porosity shared in different pore ranges [%]			
		r <0.01 µm	0.01 µm < r <0.1 µm	0.1 µm < r <1 µm	r>1 µm
UT	38.0	0.1	2.9	11.2	85.8
T5	30.1	0.8	3.4	9.7	86.2
T10	26.7	2.1	7.1	14.5	76.3

Weight variations after each cycle are reported in Fig. 1. In all treated and untreated samples, weight increased after 5 cycles, hence the contribution of salt accumulation seems to be greater than salt-induced material loss. As weight increase is lower in treated samples, it seems that consolidation was effective in limiting salt accumulation inside the samples. This is probably due to the lower porosity of the treated layer, slowing down the rate of the capillary rising flux of the saline solution and hence reducing the final amount of salts deposited inside the samples.

Salt content in untreated and treated samples is reported in Table 3. Sulphate amount is higher in untreated references, compared to T5 and especially T10-treated samples. This seems to confirm that consolidants did reduce capillary rise rate and hence salt accumulation.
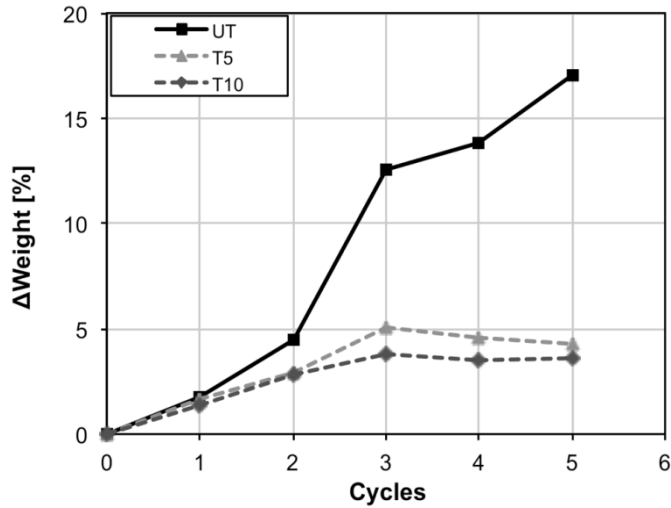
Figure 1: Weight variations in untreated and treated samples at each cycle.

Table 3: Sulphate content in untreated and treated samples after 5 cycles.

Samples	$SO_4^=$ amount [%]
UT-top	4.3
UT-bottom	3.7
T5-top	3.6
T5-bottom	2.6
T10-top	3.0
T10-bottom	2.4

In both untreated and treated samples, salts amount is higher in the top part of the samples, consistent with the higher evaporation rate in this region. In treated samples, salts are not concentrated only in the untreated volume, as would happen if the consolidated layer had acted as a clogging layer preventing their movement, but their distribution is similar to that in the untreated references (higher in the top, lower in the bottom part). Therefore, ethyl silicate did not cause any pore clogging layer and, consequently, no flaking or detachment of the treated area from the underlying part.

The influence of salt weathering on the samples' microstructure can be deduced from pore size distribution curves, reported in Fig. 2.

In untreated samples, porosity was found to be almost unaltered after weathering cycles, thus no salt-related damage (i.e. opening of micro-cracks) seems to have occurred after the cycles, despite accumulation of ~4 wt% salt (see results of IC). T5-treated samples, similarly, have suffered a very slight increase in porosity.

On the other hand, T10-treated samples, despite the lower salt content, experienced a remarkable increase in pore size distribution after the cycles. This might be due to the increase that T10 caused in the percentage of the finest pores, raising susceptibility to salt decay. As a matter of fact, the increase in the finest pores was greater in T10-treated samples than in T5-treated samples, which exhibited a much lower sensitivity to salt crystallization.

The increase in total open porosity of T10-treated samples after salt weathering suggests that some micro-cracks had opened as a result of the cycles. However, the total open porosity of T10-treated samples remained lower than that of untreated references, suggesting that some benefit was maintained after treatment and that salt decay had damaged the consolidant layer more than the sample itself.
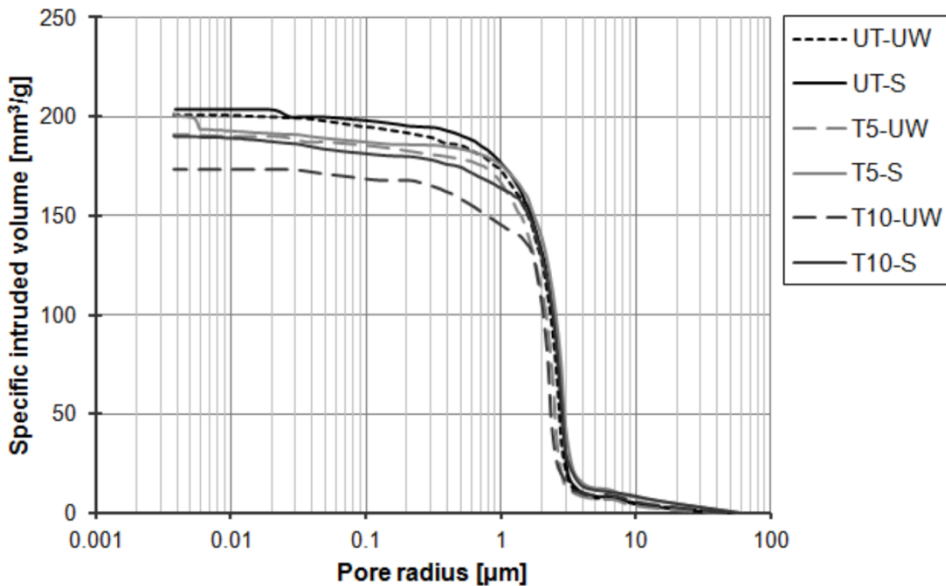

Figure 2: Pore size distribution of untreated (UT) and treated (T5 and T10) samples, both unweathered (-UW) and salt-weathered (-S), the latter after salt removal.

Further tests are currently in progress to promote a more intense decay by salt crystallization cycles and to investigate the change in mechanical properties induced by salt damage.

4 Conclusions

From the test results, the following conclusions can be derived:

- Ethyl silicate proved to be effective for the consolidation of bricks. Ten brush strokes gave better results than 5 strokes from the point of view of penetration depth and mechanical performance, hence they gave a better consolidation effectiveness. However, very good results were achieved also with the lower application number.

- Both treatments did not stop the salt transport towards the external surface and they were effective in reducing salt accumulation inside the sample by slowing down the capillary rise of the saline solution. After 5 cycles, the porosity of the consolidated bricks was still slightly lower than in the untreated samples, suggesting that some benefits from the treatments were still present. Further studies concerning mechanical properties of weathered samples are currently in progress.

- Despite T10 treatment being more effective than T5 treatment, its durability has proved to be a critical issue. The treatment was more effective in reducing salt accumulation; however, it increased brick susceptibility to salt weathering, so that no benefit is maintained after salt weathering, compared to T5 treatment. This is probably to be ascribed to the much higher increase in the fraction of smaller pores.

Acknowledgements

References

[1] Franzoni E., Pigino B., Leemann A., Lura P., Use of TEOS for fired-clay bricks consolidation, Materials and Structures, DOI: 10.1617/s11527-013-0120-7

[2] Maravelaki-Kalaitzaki P., Kallithrakas-Kontos N., Korakaki D., Agioutantis Z., Maurigiannakis S., Evaluation of silicon-based strengthening agents on porous limestones, Progress in Organic Coatings 57 (2006) 140-148

[3] Scherer G.W., Wheeler G.S., Silicate consolidants for stone, Key Engineering Materials 391 (2009) 1-25

[4] Ferreira Pinto A.P., Delgado Rodriguez J., Stone Consolidation: The role of treatment procedures, Journal of Cultural Heritage 9 (2008) 38-53

[5] Ferreira Pinto A.P., Delgado Rodriguez J., Consolidation of carbonate stones: Influence of treating procedures on the strengthening action of consolidants, Journal of Cultural Heritage 13 (2012) 154-166

[6] Franzoni E., Rising damp removal from historical masonries: a still open challenge. Construction and Building Materials 54 (2014) 123–36.

[7] G.W. Scherer, Stress from crystallization of salt, Cement and Concrete Research, 34 (2004) 1613–1624

[8] Franzoni E., Sassoni E., Graziani G., Brushing, poultice or immersion? Role of the application technique on the performance of a novel hydroxyapatite-based consolidating treatment for limestone, Journal of Cultural Heritage (2014), DOI:10.1016/j.culher.2014.05.009

[9] Franzoni E., Graziani G., Sassoni E., Bacilieri G., Griffa M., Lura P., Solvent based TEOS consolidant for stone: influence of the application technique on penetration depth, efficacy and pore occlusion, Materials and Structures (submitted)

[10] Wheeler G., Alkoxysilanes and the consolidation of stone, The Getty Conservation Institute, Los Angeles, 2005