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Enhancing the durability of historic brick masonry: the role of diammonium phosphate and chitosan in reducing salt-induced damage

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Abstract

Salt crystallization represents a serious threat to historic architecture worldwide, causing structural and aesthetic damage due to the accumulation of salts in porous building materials, such as bricks. Historic masonry is particularly vulnerable to this type of damage due to the complex interactions between salts and its porous matrix. Salt crystallization modifiers have proven to be valid candidates in reducing the detrimental effects of salt crystallization within porous materials, thereby prolonging the lifespan of historic structures. In this research, chitosan was selected as crystallization inhibitor, considering his remarkable properties in terms of sustainability and cost-effectiveness. Applied to brick samples in combination with a phosphatic treatment based on diammonium phosphate, it resulted an encouraging new solution to reduce salt crystallization damage without affecting the material's properties and hence showing a good compatibility, although further research is needed to assess the effectiveness of the chitosan-based treatments for in-the-field applications.

1. Introduction and research aim

The presence of moisture in historic walls represents one of the main problems affecting architectural heritage [1,2]. Being mainly due to the spontaneous phenomenon of capillary rising of water from the ground, moisture is responsible for various deterioration mechanisms [3,4], and salt weathering is one of the most severe [5,6]. Environmental conditions play a pivotal role in determining both the type and extent of salt damage in porous media. While efflorescence, characterized by harmless visible surface crystals, prevails in situations when evaporation from moist porous materials is slow, subflorescence, which involves disruptive internal crystal growth, thrives in warm, windy and arid climates [7,8]. In detail, repetitive dry–wet cycles increase the concentration of salts inside the pores, leading to supersaturated conditions and inducing crystallization pressure on the pore wall [9]. According to the most accepted theory about the dynamics of salt damage in confined spaces, crystallization pressure develops as the growing salt crystal approaches the pore surface, resulting in repulsive forces that prevent crystal-wall contact [10]. This disjoining pressure is crucial, and it was postulated that if this disjoining pressure was suppressed, for example by the deposition of a thin polymeric layer [11], the crystal would grow directly in contact with the pore's surface, without generating any disruptive pressure. Conversely, the presence of repulsive forces maintains a liquid film between the crystal and the pore wall, enabling the crystal to exert pressure, driven by growth, against the solid surface (Fig 1). Depending on the magnitude of the supersaturation, stress can exceed the tensile strength of the material and lead to serious damage [10,11,12]. Additionally, salt weathering significantly exacerbates the degradation and loss of building materials not only through mechanical stress, but also by enhancing the chemical dissolution of minerals in porous substrates [13].

The severity of salt-induced deterioration requires effective strategies for moisture management and salt damage mitigation, essential for the long-term preservation of architectural heritage. Addressing this challenge involves exploring various solutions, including the control of the source of salts by mitigating rising damp, which is crucial because only salts dissolved in water can enter and move through porous media [14]. However, these solutions are not always feasible and may not guarantee complete success [15]. Even considering effective solutions against rising damp, salts already present in the masonry remain difficult to completely remove through poulticing [16], and they continue to deteriorate the material. Recognizing these limitations, in the last decades researchers explored alternative strategies to protect porous materials from salt crystallization through the use of crystallization modifiers [17,18]. Crystallization modifiers are ions or molecules that can either inhibit [19] or promote [20] crystallization, affecting both the nucleation and growth phases, while also altering the shape of the growing crystals. Inhibitors can keep salts longer in solution, facilitating their transportation to the surface of the material, where they crystallize as harmless efflorescence. Conversely, promoters encourage crystallization at low supersaturation levels, preventing high crystallization pressures [21]. Different types of modifiers have been tested over the years to reduce salt damage, such as phosphonates, phosphocitrates, surfactants and polymers, with promising results [18-26]. However, several questions remain on the precise mechanisms of these modifiers when applied to building materials, requiring a deeper understanding. Another critical aspect to consider is that the application of crystallization modifiers in cultural heritage conservation must not significantly alter the materials and their properties aesthetically, physically, or mechanically, in alignment with the compatibility principle inherent in restoration practice. Moreover, the reversibility requirement poses additional challenges. As a result, recent studies focused on salt crystallization modifiers based on highly compatible biopolymers [27], among which chitosan emerged as particularly promising [27-29]. Chitosan is a biopolymer extracted from the shells of crustaceans, which has been gaining increasing attention over time due to its remarkable virtues in terms of sustainability, versatility and cost-effectiveness [30,31]. While widely known and used across a multitude of application fields, including biomedicine [32], cosmetics [33], edible coatings [34] and active food packaging [35], its potential as crystallization modifier is still in the early stages of investigation and requires further exploration. For this reason, the present research aims at deepening the understanding of chitosan's effectiveness as a crystallization inhibitor for mitigating salt-induced damage in historic architectural materials, serving as a preliminary step in a broader ongoing research project. Following previous studies [27-29], chitosan was investigated in combination with a phosphatic consolidating treatment based on diammonium phosphate (DAP), which has been found to enhance the material’s resistance and the adhesive properties of the biopolymeric coating on the substrate, thanks to the formation of a rough inorganic layer of calcium phosphates phases (mainly hydroxyapatite) from the reaction between DAP and the substrate [36,37].

The material selected for this research was fire-clay brick, chosen for its widespread use in historical masonry across Europe [38] and its significant susceptibility to salt damage due to its porous nature [39]. Modern bricks that can resemble those employed in historical architecture in terms of porosity were used, for a realistic investigation of their behavior towards moisture and salts. Different sets of samples were treated with DAP alone and with the treatment combining DAP and chitosan, while untreated control samples were used for comparison. The investigation of DAP alone was aimed at assessing its specific contribution in enhancing resistance to salt crystallization by means of its consolidating action. Conversely, chitosan alone was not investigated, as previous studies already highlighted the beneficial role of DAP in providing an anchoring substrate for chitosan [27-29].

To replicate salt damage, both treated and untreated samples were subjected to an accelerated weathering test, called “wick test”, which aims at simulating the capillary rise of salt-rich moisture in masonry, which causes salt crystallization damage in real buildings. Through detailed analysis of porosity, water absorption and crystallization patterns, the study provides interesting insights into how these treatments can extend the lifespan of historic masonry.

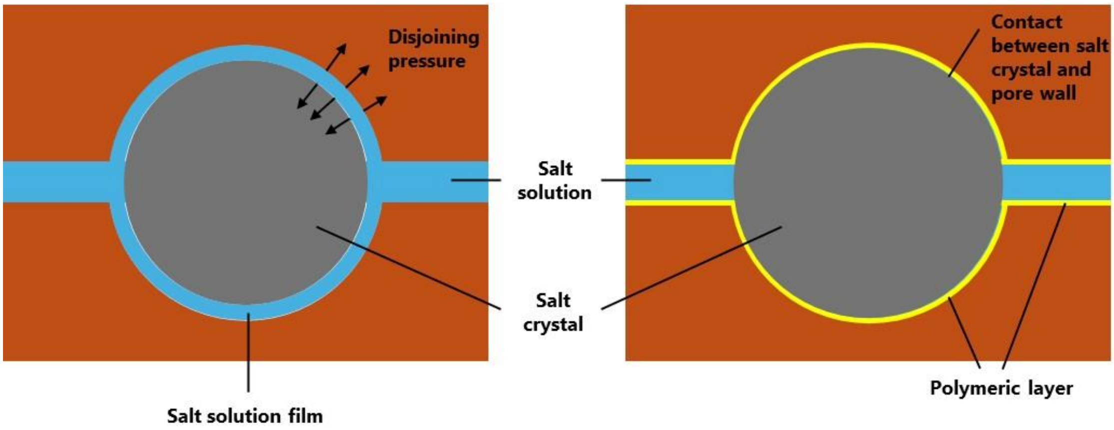


Fig 1. Left: repulsive forces arising between the salt crystal and pore wall in the material, owing to the presence of a thin solution film between them, allowing the crystal to exert pressure. Right: suppression of the disjoining pressure by application of a coating (e.g., a polymeric coatings), allowing the crystal to grow directly in contact with the pore surface, without generating pressure.

2. Materials and methods

2.1 Substrate selection

Bricks production can be considered one of the oldest industries in human history, as fired clay bricks were invented around 3500 BCE [40]. The simplicity of bricks’ manufacturing process [39] allowed for the creation of durable construction materials using basic tools and locally sourced materials, making the process both accessible and practical [41]. However, the production process varied widely depending on geographical location, local materials’ availability and technological development of different regions. Moreover, bricks exhibit significant differences in composition and properties, especially considering that the artisanal methods were empirical [42]. Raw materials composition and manufacturing parameters determined the quality and durability of bricks [43], by influencing their water absorption properties [40]. Hence, the study of historic masonry for conservation purposes is extremely challenging, especially because finding new bricks that replicate ancient ones for laboratory tests is difficult, due to present standardized mass production methods. Indeed, modern brick manufacturing focuses on uniformity and efficiency, producing bricks that are highly consistent in size, composition and performance, while traditional historic brickmaking led to highly heterogeneity bricks. In this study, solid bricks that could resemble historic ones were selected after thorough market research. These bricks, produced in Italy by IBL S.p.A. and labeled "Mattoni pasta molle Terre di Romagna classico rosso" (soft mud bricks, Terre di Romagna classic red), are handmade and this production process results in some irregularity and a porosity distribution similar to that of historical bricks often encountered in heritage architecture. As a matter of fact, the soft mud ("pasta molle") technology involves mixing clay with over 40% water by weight to achieve a desired level of workability. This high-water content results in a more porous structure compared to bricks made with other methods. The properties of the selected brick in terms of porosity were evaluated through mercury intrusion porosimetry, MIP (Thermo Scientific Pascal 140 for macropore and Thermo Scientific Pascal 240 for micropore) on three bricks and the results are reported in Fig 2 and Tab 1.

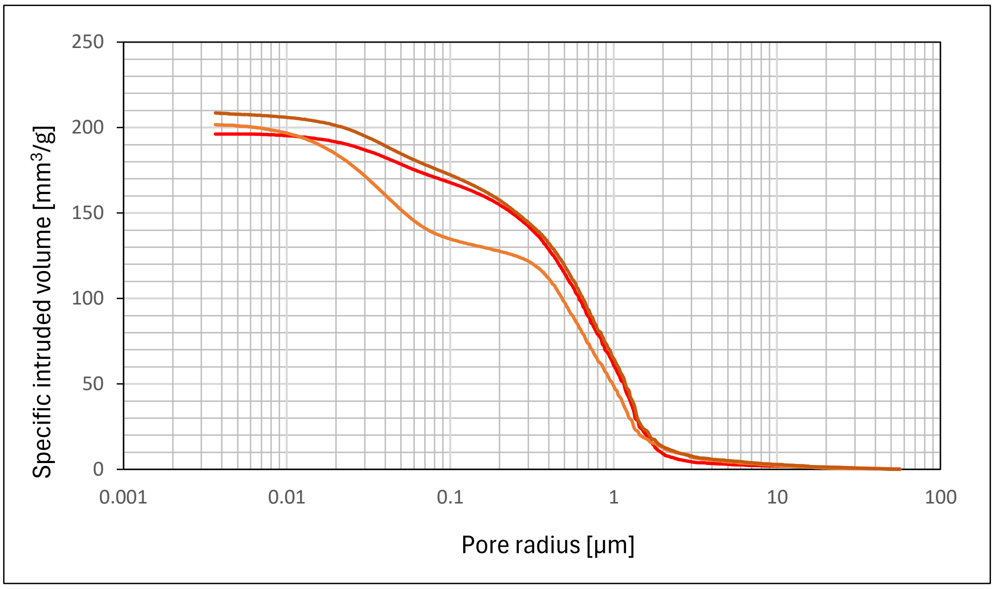


Fig 2. Pore size distribution of three samples coming from different bricks, determined by MIP.

Porosity [%]	34.93 ± 1.18
Average pore radius [µm]	0.575 ± 0.084
Total pore surface area [m^2/g]	4.111 ± 1.903
Density, ρ (g/cm^3)	1.752 ± 0.002

Tab 1. Physical characteristics of the selected bricks (average of 3 samples)

The total porosity of the selected bricks aligns with the most common range found in historical samples (25-35%), as reported by [41]. Additionally, the distribution of pore sizes in the bricks overlaps that found in another study on ancient bricks [44], particularly in the submicron range (<1 µm), which constitutes the majority of the pore volume in both cases.

A wider analysis of the effectiveness of the treatments on a broader range of bricks and other substrates will be carried out in future studies.

2.2 Treatments

Two different kinds of treatments were investigated, based on diammonium hydrogen phosphate (DAP) alone and coupled with chitosan. This methodological approach was motivated by prior research indicating synergistic effects between DAP and chitosan, particularly in enhancing the adhesive properties of the chitosan coating on the substate [27-29]. In the same previous research, the performance of chitosan alone was not so encouraging, hence it was dismissed in this study. Conversely, an evaluation of the isolated efficacy of DAP was pursued by including specimens treated exclusively with it, to provide a comprehensive understanding of the influence of each treatment on salt crystallization dynamics.

In detail, the phosphatic solution was prepared by dissolving 0.1M DAP in an aqueous solution with 0.1mM $CaCl_2$ + 10% ethanol. The addition of calcium chloride ($CaCl_2$) to the phosphatic solution provides calcium ions that facilitate the formation of hydroxyapatite (HAP), while ethanol improves coating uniformity, as suggested in previous studies [35]. The procedure for the preparation of the chitosan solution was formulated after an extensive literature survey, addressing the inherent challenges of low chitosan solubility in water. Chitosan dissolves effectively only in specific acidic solutions, with acetic acid being the most used solvent at concentrations of 0.1M or 1% (v/v) [45-48], corresponding to approximately 0.6 wt% and 1 wt%, respectively. Here, the chitosan solution was prepared by dissolving 0.2 wt% chitosan (low viscosity, Sigma Aldrich) in an aqueous solution of 0.1M acetic acid. To enhance solubility, the procedure adopted in this study involved heating the chitosan solution up to 60°C and stirring until it became clear, exploiting the accelerated chitosan solubilization at higher temperature [49]. Given the acidity of the chitosan solution ($pH \leq 3.5$), which is unsuitable for acid-sensitive substrates, NH_4OH was added to adjust pH to values in the range 5-6 at room temperature (pH 6 represents chitosan's solubility limit, according to literature [50-51]).

2.3 Samples characterization

Nine prismatic samples ($3 \times 3 \times 25$ cm^3, Fig 3) were prepared by sawing three bricks. Three samples served as untreated controls ("UT"). The remaining six samples were treated with DAP through a 24-hour partial immersion (samples laid horizontally in the solution with an immersion depth of approximately 1 cm), followed by rinsing to remove residues and drying in an oven at 40°C until constant weight. Subsequently, three of these samples received additional treatment with the chitosan solution ("D+C"), following the same procedure of immersion, rinsing and drying. The other three, treated with DAP alone, were labelled as "D".

The samples were weighed and subjected to dynamic elastic modulus measurements through ultrasonic pulse velocity test (UPV) both before and after treatments (in dry conditions) to assess the deposition of the products within them. Additionally, capillary water absorption test according to EN 15801:2010 [52] was performed on one sample for each treatment, before and after the treatments, to evaluate any significant alterations in water transport behavior. As the representativity issues are always important when dealing with bricks, whose heterogeneity is well known, these concerns were mitigated by performing the capillary absorption test on exactly the same samples before and after the treatment application. Therefore, the results are considered reliable enough to evaluate any changes induced by the treatments.

Additionally, to assess the compatibility of the treatments from an aesthetic point of view, the color of the treated and untreated samples was measured using a NH310 High-Quality Portable Colorimeter, determining the color change induced by the treatments. The L*, a*, b* colorimetric coordinates were used and the total color difference (ΔE*) was calculated according to the CIE76 formula [53].

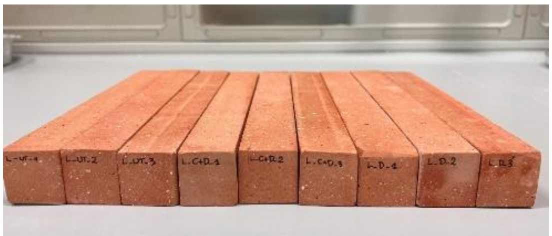


Fig 3. Brick samples selected for the experiment (3×3×25 cm³)

2.3 Salt weathering procedure: "Wick test"

Different accelerated degradation tests are available to assess in laboratory the resistance of construction materials to salt crystallization damage. A commonly used technique involves exposing samples to repeated wetting and drying cycles, consisting in their full or partial immersion in salt solutions followed by drying under various conditions [54]. While these procedures are useful for quickly assessing porous materials resistance to salt crystallization, the prescribed conditions may be excessively aggressive, as it was suggested for the European standard EN 12370 [55], potentially leading to damage patterns that are unrealistic and significantly different from those observed in practice. Recently, a new protocol proposed by RILEM TC 271-ASC introduced a novel accelerated method based on a two-stage procedure: an accumulation phase, where salts fill the pores of the very surface layer of the samples but do not cause damage yet, and a propagation phase, where repeated cycles of salt dissolution and crystallization lead to damage initiation and propagation [56,57]. This procedure was successfully tested on different stones and bricks in a Round Robin Test [56], but it has not been used yet for the investigation of treated materials, i.e., in samples where the bulk material and the treated surface layer may exhibit different properties. Hence, in this study, a test involving a continuous rise of water and salts through the material was selected, as it was considered particularly suitable to simulate the occurrence of rising damp in masonry walls. This test, which is called "wick test", was performed in laboratory according to the procedure developed for the first time by Goudie in 1986 [58] and refined based on the recent experiences of other researchers [59]. In particular, two prismatic brick samples for each treatment condition ("UT", "D", "D+C") were vertically immersed in a beaker filled with 200 ml of 10 wt% sodium sulphate solution, until its complete absorption (~8 days) in laboratory conditions (T = 22 ± 2 °C; RH = 50 ± 5%). A layer of melted paraffin was poured on the solution inside the beaker to prevent its evaporation during the test. At the end of the test, the deterioration of the prisms was investigated, selecting for this purpose the final assessment method suggested by the RILEM TC 271-ASC guideline [53], which involves the gently brushing of the samples and the collection of efflorescence and debris. This characterization procedure was selected as it provides a detailed insight into the deterioration suffered by the samples. In brief, the debris collected at the end of the wick test was initially dried in an oven at 40°C until reaching a constant mass and then cooled in a desiccator for at least 2 hours before weighing (weight labelled as d_1). Then, the debris was placed in a glass beaker with deionized water (water mass at least ten times higher than the debris mass), stirred manually and left for 24 hours at room temperature to ensure complete dissolution of the salts. This dispersion was filtered through a filter paper designed for medium to fast filtration and previously dried at 40°C for 24 hours, then cooled in a desiccator for at least 2 hours before recording its weight (m_{paper}). The filter paper, along with the retained material, was dried at 40°C until constant mass, cooled in a desiccator for 2 hours and the cumulative mass recorded ($\mathrm{m_{loss\ cum}}$). The material loss was calculated by subtracting the mass of the dry filter paper from this cumulative mass ($d_2 = \mathrm{m_{loss\ cum}} - m_{paper}$). The weight of the salt efflorescence was then determined by subtracting the material loss from the initial debris mass as:

$m_{effl} = d_1 - d_2$

The degradation was also assessed through visual and photographic observations during the test, to document the extent and characteristics of the damage. These qualitative observations complemented the quantitative data, capturing details such as salt distribution patterns and surface texture changes that quantitative measurements alone might not fully reveal.

3. Results

3.1. Samples characterization

The mass of the samples slightly increased after both DAP treatment alone and DAP-chitosan treatment, as shown in Tab 2. These results indicate that a certain absorption and deposition of the coatings inside the material occurred. However, it is worth noting that, although the outcomes are consistent with previous studies [27-29], the increase observed in this case is significantly higher. This variation can be attributed to several factors, including the higher concentrations of the solutions used with respect to previous studies (0.2 wt% chitosan versus 0.05 wt%). Moreover, the types of substrates selected in the two studies were different, as this research was performed on bricks, which exhibit higher porosity and different microstructure compared to the limestones used in the previous studies [27], and this may lead to deeper penetration and greater retention of the treatments. Nonetheless, despite the mass increase being higher than in other studies, it remains very low, suggesting that the treatments do not significantly alter the porosity of the material. This is a very important observation, as the risk of pore clogging is one of the main problems for compatibility. However, a detailed interpretation of the measured mass increases after the two treatments is challenging, as the values observed are extremely small and in fact comparable to their standard deviation (Tab. 2). Additionally, a certain level of variability in the mass changes can be observed, suggesting that the natural variability of the samples slightly influences the absorption of the treatments. The fact that the untreated samples exhibit the highest mass (Table 2) was considered accidental and was probably related to some heterogeneity of brick and/or imperfection in the samples' cutting and hence geometry. In fact, this difference is very limited and comparable with the standard deviations for this parameter, so it was considered uninfluential in the tests.

UPV test showed an increase in dynamic elastic modulus (Ed) after treatment (Tab 3), which aligns with the observed mass gain in the samples. In particular, the most pronounced increase in the dynamic elastic modulus was observed for the combined chitosan and DAP treatment (D+C) and this could be attributed to several factors. Although the mass gain for the D+C treatment is lower compared to the gain achieved with DAP alone (D), the observed enhancement in the dynamic elastic modulus might still suggest effective material deposition and reinforcement. It is possible that the coating obtained by combining DAP and chitosan offers a more continuous path for UPV transmission. Furthermore, there could be a synergistic effect between the two treatments that enhances the material’s mechanical properties beyond what is suggested by mass gain alone. Thus, the combined treatment seems to exhibit better physical properties, potentially due to improved interaction between the two treatments. An increase in the UPV values, for instance, could indicate enhanced material “integrity” (in terms of continuity of the ultrasonic transmission pathway) and/or increased mechanical strength. In either case, the combined treatment seems to have a positive outcome.

Samples	W_{dry} [g]	W_D [g]	W_{D+C} [g]	$\Delta W_{(D - dry)}$ [g]	$\Delta W_{(D+C - dry)}$ [g]
UT	419.58 (±5.00)	-	-	-	-
D	417.97 (±9.59)	419.32 (±9.64)	-	+1.35 (±0.95)	-
D+C	409.33 (±5.68)	409.92 (±5.67)	410.25 (±5.70)	+0.60 (±0.04)	+0.92 (±0.05)

Tab 2. Sample mass before and after treatment, in dry conditions (averages from three samples per treatment condition)

Samples	E_d [GPa]		ΔE_d treated [GPa]
	Untreated	Treated	
UT	11.33 (±0.55)	-	-
D	11.38 (±0,76)	11.72 (±0,53)	+0.34 (±0.24)
D+C	10.20 (±0.80)	10.79 (±0.84)	+0.59 (±0.08)

Tab 3. Dynamic elastic modulus before and after treatment, in dry conditions (averages from three samples per treatment condition).

The analysis of water absorption before and after the DAP and DAP+chitosan treatments reveals a very limited effect on the material's water transport properties in terms of capillary water absorption coefficient (AC), as reported in Table 4. The AC for the untreated and D samples are basically overlapping, indicating that the DAP treatment alone does not alter the material's microstructure, as expected [27-29]. In the case of the D+C sample, there is a very slight reduction in water absorption rate, as AC value decreases from 0.23 to 0.20 kg/m$^2\sqrt{s}$, aligning with expectations that the treatment should not significantly impact the material's inherent properties.

The color change (ΔE*) for both D and D+C treatments with respect to untreated bricks is reported in Table 5. The values are below the threshold commonly accepted for conservation purposes, i.e. ΔE*=5 [60]. This indicates that the treatments had a minimal impact on the visual appearance of the specimens, preserving their original aesthetic qualities.

Samples	Treatments	AC [kg/(m^2·√s)]
D	Before	0.24
	After	0.23

D+C	Before	0.23
	After	0.20

Tab 4. Comparison between the D and D+C samples before and after treatments in terms of capillary water absorption rate (AC).

Treatment	ΔE*
D	1.27 ± 0.49
D+C	4.02 ± 0.44

Tab 5. ΔE* values calculated comparing treated samples with untreated ones, based on L, a*, b* colorimetric coordinates (average of three samples for each condition).

3.2 Wick test

The weight changes of the samples at the end of the test (after brushing away the efflorescence) are reported in Figure 4-left, where a general increase was observed, due to salt accumulation within the porous bricks. Bricks treated with DAP+CHIT showed lower weight increase compared to the untreated ones, indicating that the combined treatments may have mitigated harmful sub-efflorescence, promoting less detrimental efflorescence instead, which spontaneously fell (and were collected as debris). This observation is supported by the results of the dynamic elastic modulus increase at the end of the test (Figure 4-right). The untreated samples exhibited a more significant increase in the elastic modulus, likely due to salt accumulation within the material, which may have influenced the ultrasonic wave propagation speed, leading to higher values. In contrast, the treated bricks showed lower increase in the elastic modulus, suggesting that the formation of subflorescence within the material was reduced and the treatments encouraged the salts to crystallize as surface efflorescence instead.

The analysis conducted on debris and efflorescence removed from the samples at the end of the test supports the earlier findings (Figure 5 and Table 6). The salt fraction observed in the untreated samples was lower compared to the treated ones, and the samples that received the combined treatment of DAP and chitosan exhibited the highest amount of salts in the debris. This suggests that the synergistic action of DAP and chitosan may have facilitated the formation of efflorescence rather than subflorescence. The solid fraction of debris collected from untreated samples was higher than that removed from the treated ones, indicating that the treatments effectively reduced material loss. Although there was only a slight difference between treated and untreated samples, the results are still positive, demonstrating that the treatments helped preserving sample integrity by reducing degradation. The improvement in salt resistance of bricks with DAP alone can be attributed to its role in increasing tensile strength and promoting a rough pore surface that facilitates capillary flow to the exterior, thereby fostering efflorescence over harmful subflorescence [25], as evidenced by the higher amount of efflorescence observed with DAP compared to untreated bricks.

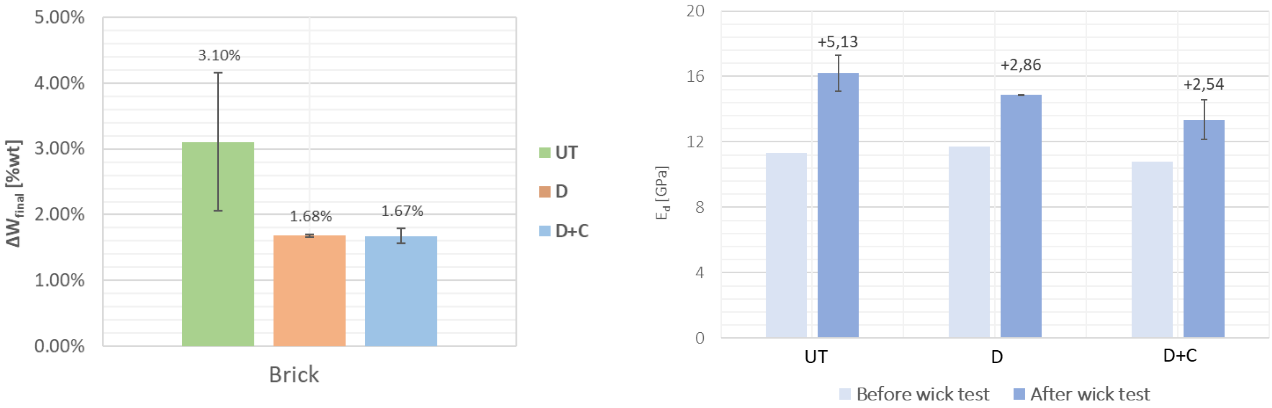


Fig 4. Left: weight increase of the samples after brushing at the end of the wick test, using the initial weight as reference; right: dynamic elastic modulus after the wick test and subsequent brushing.

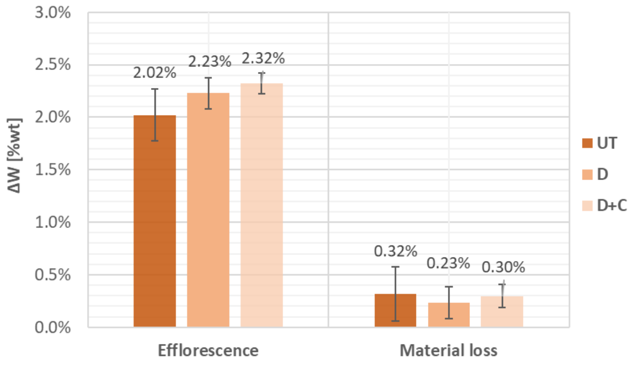


Fig 5. Weight percentages of the salt and solid fractions in the debris, based on the weight of the brushed prisms.

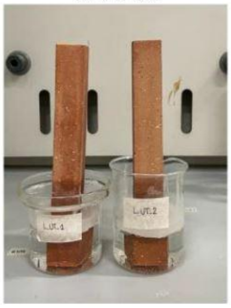
Samples	$W_{efflorescence}$ [g]	W_{loss} [g]
UT	8.73 (±1,01)	1.37 (±1,12)
D	9.58 (±0,40)	0.99 (±0,62)
D+C	9.74 (±0,28)	1.24 (±0,45)

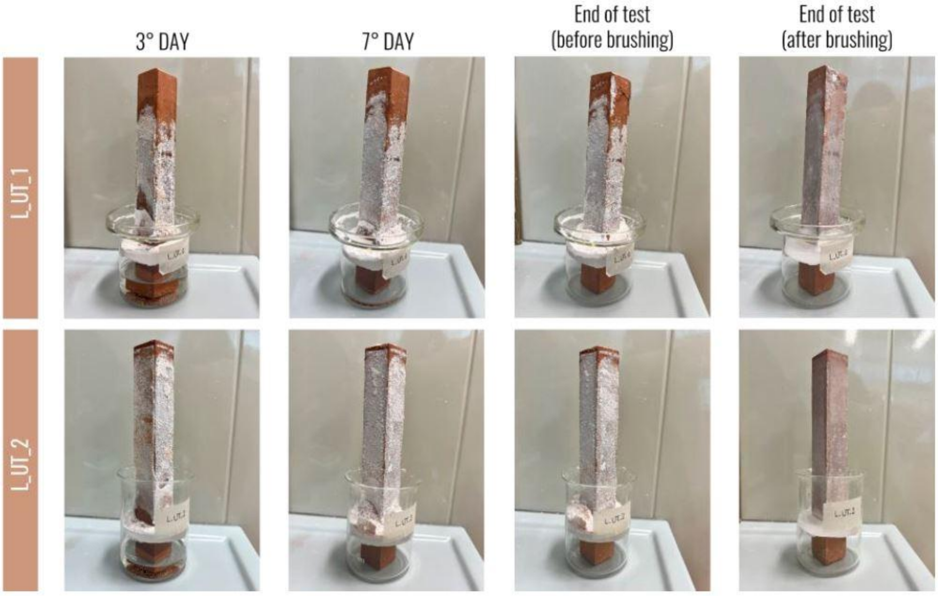
Tab 6. Weight of the efflorescence and material loss after the wick test.

Regarding the visual analysis during the test, it was possible to observe the process of efflorescence formation on the surface of the samples, resulting from the continuous absorption and simultaneous evaporation of the saline solution. After brushing off debris and efflorescence, a white film was observed on the surface of the treated and untreated samples, but the degradation of the brick substrates was very limited. Figure 6 shows the evolution of the brick prisms, comparing their condition at the beginning, during and at the end of the weathering test, both before and after brushing.

L_UT

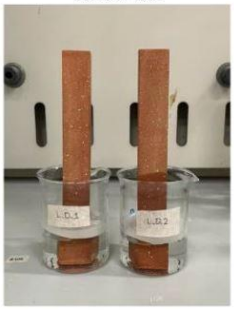
Start of test

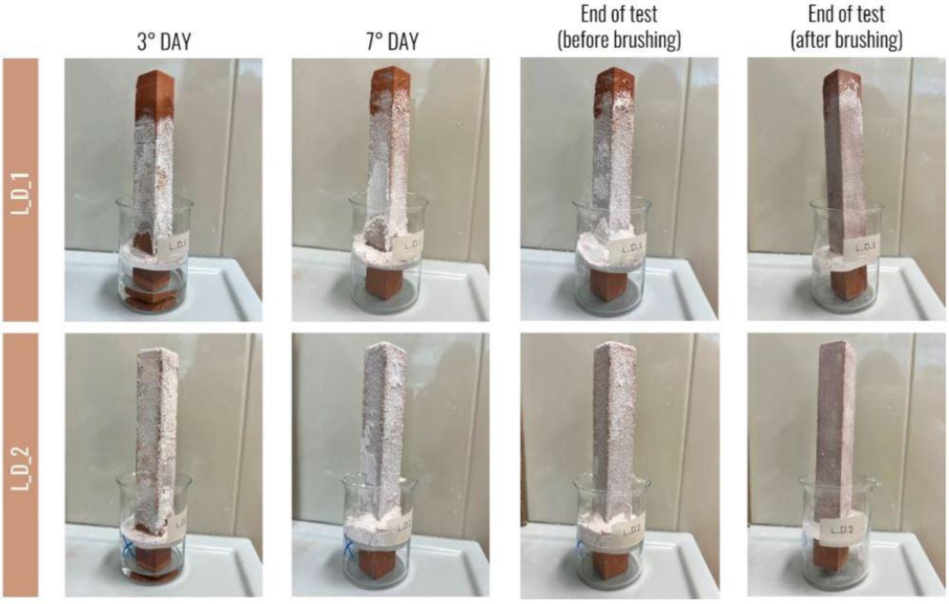




L_D

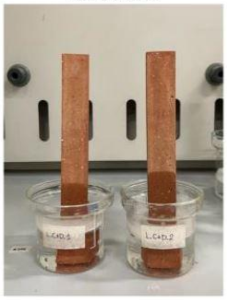
Start of test





L_C+D

Start of test



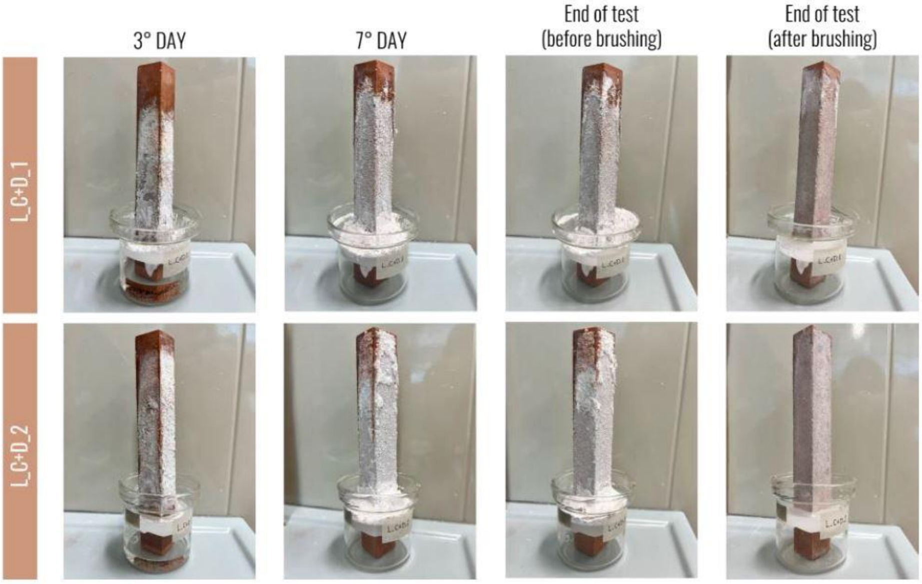


Fig 6. Evolution of brick samples degradation during the wick test.

Further analyses, such as SEM observations of the crystalline structure and distribution of efflorescence, could provide additional insights into the transition from sub-efflorescence to external efflorescence and the effects of treatment on crystal size within the pores.

4. Conclusions

The study allowed to evaluate the performance of chitosan and diammonium phosphate (DAP) treatments in mitigating salt-induced damage in highly porous substrates such as bricks.

Both treatments were successfully deposited within the bricks, as shown by the increase in mass and dynamic elastic modulus, without significantly altering the water transport properties of the substrate. Additionally, colorimetric analysis confirmed that the treatments caused changes within the accepted threshold for conservation purposes. These findings underline the compatibility of the products with the brick substrate, a crucial aspect in the conservation field. However, future analyses will be aimed at investigating the distribution and nature of the chitosan coating deposited on pore walls.

The wick test results suggested that the treatments reduced salt-induced damage. The observed decrease in material loss and possible shift towards less harmful efflorescence, rather than disruptive sub-efflorescence, supports the efficacy of the treatments. This was indicated by a higher saline fraction and reduced material loss in treated samples compared to untreated ones. Despite these promising results, their variability points to the complexity of simulating salt damage and assessing the treatments performance in laboratory. Further investigations will be addressed to understand the role of factors that might affect the performance of the treatments, such as sample porosity, material heterogeneity and environmental conditions. The best application method, the pH and concentration of the solutions, the interactions between the treatments and the substrate and the long-term effects of these treatments on the durability of historical building materials are further aspects that need full elucidation in view of these treatments' exploitation in conservation practice.

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