



Resistance of consolidated lime mortars to freeze–thaw and salt crystallization cycles by different accelerated durability tests

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Received: 9 August 2023 / Accepted: 16 April 2024
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Abstract The present study aimed at evaluating the performance of untreated and consolidated lime mortars, in terms of durability and possible “delayed incompatibility” of the consolidants. Lime mortars samples were treated by an aqueous solution of diammonium hydrogen phosphate (DAP treatment) and a dispersion of nanolimes (NL treatment). The samples were then subjected to accelerated ageing by different methods: (1) freeze–thaw cycles; (2) salt crystallization cycles based on the European standard EN 12370 (often considered as highly aggressive); (3) salt crystallization cycles according to a new recommendation proposed by the RILEM TC 271-ASC (designed to provide less aggressive and more reliable ageing). The results of the study showed that the DAP-based treatment was able to significantly reduce damage caused by freeze–thaw cycles and salt weathering cycles by the RILEM procedure. In the case of salt weathering by the EN procedure, some risk of “delayed incompatibility” was highlighted for DAP, which can be considered an outcome of the combination between the salt weathering procedure itself and the consolidating treatment. For both freeze–thaw and salt weathering by either procedure, the residual mechanical properties of DAP samples at the end of

the cycles were significantly higher than those of the untreated references and of the NL samples, for which the effects of the NL treatment were very modest.

Keywords Consolidation · Ammonium phosphate · Hydroxyapatite · Nanolimes · Durability · Accelerated weathering

1 Introduction

Consolidation of lime mortars used as renders, plasters and bedding mortars in masonry is an open challenge. Consolidation consists in the application of products (e.g. solutions or dispersions) that should penetrate the deteriorated substrate and reach the non-deteriorated part. After hardening, the consolidant should seal the tip of the cracks formed as a consequence of deterioration, thus bonding the grains more effectively, increasing the cohesion of the deteriorated material and anchoring it to the underlying sound part. As a result, the service life of the treated substrate should be increased. In doing so, consolidating products should simultaneously meet important requirements [1–3]:

- *Effectiveness*, i.e. ability to penetrate in depth (in the case of deteriorated lime mortars, down to several centimeters from the surface [4]) and provide mechanical strengthening, without creating

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a superficial layer of a hard material over a weak substrate.

- *Compatibility*, i.e. the properties of the consolidated material should match as closely as possible those of the original substrate, including both aesthetic features (e.g. color and gloss) and physical–mechanical properties (e.g. pore size distribution, water and water vapor transport, thermal expansion, mechanical properties) [1, 4–7]. As a matter of fact, any consolidation treatment necessarily alters the pore system, since pores are partially filled with new solid phases that result from the hardening process of the liquid consolidants. Alterations in open porosity and pore size distribution may lead, on the one hand, to reduced permeability to water and water vapor (which may cause damage in case water or saline solutions are trapped behind the consolidated later) [2, 3, 8] and, on the other hand, to increased sensitivity to freeze–thaw and salt crystallization cycles (because the smaller the pore, the higher the crystallization pressure in the pore when water freezes or salts crystallize from saline solutions [9, 10]). These potentially negative alterations to the pore size system should be compensated by the increase in mechanical properties, thus ensuring a final higher resistance to deterioration processes after consolidation. Actually, a very high increase in mechanical properties may be counterproductive, as it may lead to mechanical incompatibility between the softer, weaker substrate and a stiffer, stronger overlying consolidated part. To avoid “delayed incompatibility” (i.e. the failure of the consolidation treatment because damaging effects appear in the medium-long term), defining what are the maximum alterations allowed after consolidation (i.e. maximum increase in mechanical properties, maximum reduction in open porosity, etc.) is a very important but also very challenging task [1, 7]. For instance, maximum increases in compressive strength by 25% for consolidated stones and by 50% for repair mortars used on traditional masonry have been proposed [1].
- *Durability*, i.e. the ability of the treatment to maintain its function over time, thus prolonging the service life of the consolidated substrate [7, 11]. This depends, on the one hand, on the durability of the consolidant itself (e.g. its water solubility)

and, on the other hand, on the aggressiveness of the environment [12].

- *Reversibility*, i.e. possibility to remove a treatment after its application [4, 8]. However, in the case of inorganic products, it is impossible to remove the hardened consolidant (its low solubility is actually considered a positive aspect to achieve good durability), so reversibility is only theoretically possible in the case of polymeric materials, which however have shown severe durability issues [13]. As a result, the reversibility requirement is often substituted with the requirement that the treated substrate remain retreatable, i.e. it should be possible to treat again the consolidated material with the same or another product.

Among the products for consolidation of carbonate substrates (including lime mortars [14]), nanolimes and ammonium phosphate have received considerable attention in recent years.

Nanolimes, initially proposed for conservation of frescoes [15], are dispersions of $\text{Ca}(\text{OH})_2$ nanoparticles in alcohol (typically isopropanol or ethanol) [16]. After the application, the nanoparticles react with atmospheric CO_2 and transform into calcium carbonate. Following initial tests on frescoes [15], successful use of nanolimes for consolidation of wall paintings, lime-based mortars and carbonate stones has been reported [17, 18]. As a result, in the technical data sheets of commercial nanolimes ideal compatibility with carbonate stones is stated [19]. A limitation of this treatment is the use of alcohol for the nanoparticle dispersion, which is needed to avoid agglomeration of the nanoparticles. In fact, on the one hand, the use of alcohol favors the formation of metastable phases of calcium carbonate (namely, aragonite and vaterite), which slows down the formation of the most thermodynamically stable phase (calcite) that is responsible for the highest mechanical improvement [18]. On the other hand, the use of alcohol for the nanolime dispersion also increases the environmental impact of this consolidating treatment [20]. Furthermore, the consolidating effect is often limited to the surface of the treated material, because, after penetration into the substrate, the nanoparticles tend to be transported back towards the surface during drying, due to the rapid evaporation of the organic solvent [18].



The DAP-based treatment, originally proposed for stone consolidation [21–23], has later been explored for a variety of substrates, including lime mortars [24–26]. The treatment is based on the idea of reacting the calcium-rich substrate with an aqueous solution of a phosphate precursor (diammonium hydrogen phosphate, DAP, $(\text{NH}_4)_2\text{HPO}_4$) [21]. After a few hours of reaction, a new mineral is formed, namely hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which is the main mineral constituent of teeth and bones [23, 25]. Thanks to the low viscosity of DAP solutions, this treatment is able to deeply penetrate into the substrate and significantly improve its mechanical properties, as newly formed HAP increases the bonding among the grains.

Previous comparative studies performed on lime-based renders applied onto bricks [26] and on lime-based mortars artificially contaminated with sodium sulfate [24] have shown that DAP generally exhibits higher effectiveness than nanolimes, even when salts are already present in the pores of the treated substrate [24]. Notably, the strengthening effect of DAP is obtained after curing for just 24 h, while curing for 4 weeks is recommended for nanolimes. Both consolidants are generally compatible with the substrate, in terms of color change after treatment and maintenance of the hydrophilic behavior [24, 26], so that issues arising from hydrophobization of the substrate are prevented.

Because both consolidants are responsible for some alteration in the pore size distribution of the substrate, previous studies [24, 26, 27] have investigated whether consolidated lime mortars may suffer from “delayed incompatibility”, i.e. a decrease in their resistance to weathering cycles (freeze–thaw, salt crystallization) due to unfavorable alterations in the pore system and in mechanical properties after consolidation. However, the accelerated ageing procedures adopted in previous studies have been criticized in the literature for being scarcely reliable.

In particular, in the case of resistance to salt crystallization, the European standard 12,370 [28] has been criticized for being too aggressive, as it involves cycles of immersion in a highly concentrated (14 wt%) solution of $\text{Na}_2\text{SO}_4 \bullet 10\text{H}_2\text{O}$ [29], which does not exist in practice [30]. As a result of such high aggressiveness, strong damage is reached quickly, which is convenient for the laboratory activity but not necessarily representative of the real conditions in the

field. In fact, the kind of damage obtained by using such highly concentrated solution of $\text{Na}_2\text{SO}_4 \bullet 10\text{H}_2\text{O}$ often does not reproduce the type of damage occurring in the field [31, 32]. A realistic salt content of 1–2 wt% $\text{Na}_2\text{SO}_4 \bullet 10\text{H}_2\text{O}$ with respect to the dry specimen can be obtained by using less concentrated salt solutions, thus achieving an effective and reliable test [33–35].

Given the above-described limitations, the scientific community has been working on the development of a more reliable test. Among other efforts, a new test method has been recently proposed by researchers working within the RILEM TC 271-ASC [36], which was created with the aim of developing a new accelerated but still reliable salt crystallization test for porous building materials, as detailed in § 2.3.2.

Similar to the case of salt crystallization cycles, also in the case of freeze–thaw cycles European standards do exist for natural stones (EN 12371 [36]) and agglomerated stones (EN 14617–5 [37]), and many other national standards do exist, but still different testing procedures are often adopted in literature [38–43], for economic and/or scientific reasons (e.g. the different properties of the investigated material).

In the light of what discussed above, the present study aimed at assessing:

1. The resistance of lime-based mortars consolidated with DAP and nanolimes to freeze–thaw and salt crystallization cycles, so as to identify whether risks of “delayed incompatibility” do exist;
2. The effects of two alternative methods to test the salt resistance of porous substrates (namely a slightly modified version of the European standard 12,370 [28] and the test recently proposed by the RILEM TC 271-ASC [36, 44, 45]), so as to highlight the pros and cons of each method.

2 Materials and methods

2.1 Mortar specimens

The mortar specimens were prepared using slaked lime by Colacem, Italy (CL 70-S) and calcareous aggregates (average CaCO_3 content of 95 wt%, maximum particle size of 4 mm). A binder-to-aggregate

ratio of 1:2 v/v (0.41 w/w) and a water-to-binder ratio of 1:1 v/v (0.45 w/w) were adopted. After preparation in a Hobart mixer, the fresh mortar was poured in purposely-built impermeable molds ($30 \times 20 \times 160 \text{ mm}^3$), then immediately unmolded. After curing in laboratory conditions ($\text{RH} = 50 \pm 5\%$, $T = 21 \pm 2 \text{ }^\circ\text{C}$) for a total of 7 months to ensure carbonation, the specimens were hand sawn to obtain $30 \times 30 \times 20 \text{ mm}^3$ samples.

Even though consolidants should be ideally tested on deteriorated specimens, that exhibit the type of deterioration that consolidants are expected to fix (e.g. cracks, powdering, material loss), in the present study no preliminary artificial weathering was performed on the mortar specimens, to make sure that the samples could be safely managed in laboratory operations without breaking. The effects of the consolidants were hence evaluated in terms of ability to increase the substrate mechanical properties and ability to reduce the decrease in mechanical properties as a consequence of ageing, compared to the untreated references.

2.2 Consolidating treatments

The two consolidants were applied until apparent refusal, intended as the condition when the substrate remains wet for more than 1 min [46] which is no longer able to absorb the liquid product. Application until apparent refusal, with the aim of maximizing the consolidant effectiveness, is recommended in the technical data sheet of the commercial nanolimes used in this study [19] and has been frequently reported in the literature also for DAP [25]. Even though the two consolidants have a different concentration of the active principle (396 g/L for DAP vs 5 g/L for NL, as detailed in the following), so that application until apparent refusal leads to different amounts of active principle being introduced into the substrate, still carrying out a comparison in these conditions is most representative of real conditions in the field. Indeed, the alternative for practitioners would be to treat a given substrate by saturation with either one of the two consolidants, which corresponds to the conditions adopted in this study. Application was performed by brushing, as this is a common technique frequently adopted in the field.

For each treatment, the product uptake was determined by weighing the samples before (dry

condition) and at the end of the consolidant application (wet condition).

2.2.1 Ammonium phosphate (DAP)

For the DAP treatment, diammonium hydrogen phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$), kindly supplied by CTS s.r.l. (Italy), was used. According to the procedure originally proposed for consolidation of porous limestone [47], the treatment was applied in two steps: (i) first, a 3 M (396 g/L) DAP aqueous solution was brushed onto one of the $30 \times 30 \text{ mm}^2$ faces of the samples until apparent refusal, reached after 40 brush strokes; the samples were then wrapped with a plastic film to prevent evaporation and left to react for 24 h, then unwrapped, rinsed with water and left to dry at room temperature; (ii) second, a poultice of cellulose pulp and limewater (i.e. a saturated solution of calcium hydroxide), adopting a 1:4 w/w ratio, was applied onto the treated surface for 24 h (wrapping again the samples to prevent evaporation), then the samples were unwrapped and the poultice was left to dry on the samples. The limewater poultice was aimed at promoting HAP formation by supplying additional calcium ions and at removing unreacted DAP during drying [47]. Before testing, the samples were kept in laboratory conditions ($\text{RH} = 50 \pm 5\%$, $T = 21 \pm 2 \text{ }^\circ\text{C}$) for 1 month, corresponding to the curing time required for the nanolime-based treatment.

2.2.2 Nanolimes (NL)

The commercial product Nanorestore Plus® Ethanol 5, kindly supplied by CTS s.r.l. (Italy), was used. This is a dispersion of $\text{Ca}(\text{OH})_2$ nanoparticles in ethanol with a concentration of 5 g/L. Similar to the DAP treatment, mortar samples were treated by brushing on one of the $30 \times 30 \text{ mm}^2$ faces until apparent refusal (40 brush strokes). According to the procedure recommended in the product technical data sheet, the brushing application was performed through a sheet of Japanese paper to avoid surface whitening. At the end of the consolidant application, a poultice of cellulose pulp and deionized water (1/4 w/w) was applied onto the treated surface, again following the indications on the product technical data sheet. Once dry, the poultice was removed and the samples were left to cure in laboratory conditions ($\text{RH} = 50 \pm 5\%$, $T = 21 \pm 2 \text{ }^\circ\text{C}$) for 1 month before testing.



2.3 Accelerated ageing procedures

Untreated and treated samples were subjected to the ageing procedures described in the following. A summary of all the conditions considered in the study is reported in Table 1. For each condition, at least 3 replicate samples were tested. For each procedure, changes in weight and dynamic elastic modulus (cf. § 2.4.3) were assessed as a function of the number of cycles, while the residual compressive strength was determined by double punch test at the end of the cycles (§ 2.4.4).

In the case of non-destructive measurements (weight and dynamic elastic modulus), the parameters were determined before and after cycles, so the variation occurred in each specimen was first calculated and then the variations in the three specimens were averaged. The results are hence expressed in terms of average value and corresponding error bars.

Differently, in the case of destructive tests (compressive strength), it was not possible to test the same sample before and after ageing, thus an average value of three replicates was determined for the condition before ageing and an average value for the condition after ageing, then the corresponding variation was calculated (without error bars, as it is the difference between average values).

2.3.1 Freeze–thaw cycles

Freeze–thaw cycles (“FT cycles”) were performed by combining the European standards EN 12371 [37], EN 14617–5 [38] and the Italian standard UNI11186 [48], like in previous studies [27, 49]. The adopted procedure consisted in first saturating the samples by partial immersion in deionized water for 72 h and then performing 10 freeze–thaw cycles as follows. The water-saturated samples were placed in a freezer at $-20\text{ °C} \pm$ for 2 h, then immersed in water at 20 °C

for 2 h. After each cycle, the samples were dried in oven at 40 °C for 72 h and then characterized. In total, 10 cycles were carried out.

Keeping the samples at -20 °C for 2 h, as suggested by the Italian standard UNI 11186 [48], was regarded as sufficient to ensure freezing of water inside the pores, considering that, according to the Kelvin law, the freezing temperature decreases in pores with smaller size (e.g., a temperature of -10 °C is sufficient for water to freeze in pores larger than $0.003\text{ }\mu\text{m}$ [50]) and also considering that the mortars used in this study had average pore radius ranging between 0.04 and $10\text{ }\mu\text{m}$, as shown in § 3.3.1. Moreover, because in the present study the size of the specimens was smaller than that suggested by EN 14617–5 [38], where a minimum temperature of -20 °C is also recommended, freezing in the whole volume of the specimens is expected.

2.3.2 Salt crystallization cycles

Salt-crystallization cycles were performed based on the two cited methods:

European standard EN 12370:2001 (“EN cycles”) [28]:

The stated scope of this standard is to determine the relative resistance of natural stones with an open porosity $> 5\%$ to the damage caused by salt crystallization. According to the standard, samples (cubes with 40 mm side) should be subjected to cycles of immersion into a saline solution (renewed each time) and drying, the mass change being recorded.

Even though total immersion is recommended by the cited standard, in the present study partial immersion was preferred (following previous studies [49, 51]). In this way, it was possible to replicate the situation experienced in the field, where saline solutions enter porous building materials by capillary rise from the ground and exit by evaporation

Table 1 Labelling of the treatment conditions and of the ageing procedures

Condition	Label	Followed procedure
Untreated	UT	–
DAP	DAP	–
Nanolimes	NL	–
Freeze–thaw cycles	“FT cycles”	Combination of [36, 37, 48]
Salt crystallization cycles	“EN cycles”	Modified version of [28]
	“RILEM cycles”	[36]

through the external surface (i.e. the treated one). Thus, it is possible to estimate whether the consolidated surface layer could act as a barrier, impeding the exit of the saline solution and causing salt accumulation below the treated layer. On the contrary, in case total immersion were used, the saline solution would enter the samples through the consolidated layer, which is the opposite of what happens in the field, and which may cause unrealistic redistribution of the salts within the samples.

Therefore, for each cycle the mortar samples were partially immersed in a 14 wt% aqueous solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ for 2 h, placing the samples with the $30 \times 30 \text{ mm}^2$ faces horizontal and adding solution until half of the sample thickness (20 mm) was reached. After partial immersion for 2 h, the samples were dried in oven at 40°C for 20 hours, then cooled down to room temperature for 2 hours and finally characterized in terms of changes in weight and dynamic elastic modulus. A drying temperature of 40°C was selected, instead of drying at 105°C as foreseen by the EN 12370 [28], to avoid thermal damage that may occur in the substrate at high temperature. Afterwards, the next cycle was started. After 10 cycles, the samples were desalinated as described in § 2.4.1 and then characterized.

Recommendation by RILEM TC 271-ASC (“RILEM cycles”) [36]:

The stated purpose of this procedure is to assess the durability of porous building materials (stones and stone-like porous materials) against salt crystallization, by accelerating the deterioration process without significantly altering its mechanism [36]. In particular, the procedure is designed to replicate the situation of near-surface damage that occurs in the field as the result of saline solution transport into porous materials by capillary rise and evaporation. The procedure has been validated for single materials (stones and bricks) with open porosity between 13 and 50%, but it can be adapted to combinations of materials. Reasoning that damage from salt crystallization consists in a phase of salt accumulation within the pores of the material and then a phase of damage propagation [36, 45, 52], according to this recommendation samples should first let absorb saline solution by capillarity (“accumulation phase”) and then subjected to repeated wetting/drying cycles with water (“propagation phase”), the mass change being recorded.

First, the samples were sealed along the lateral surface with Parafilm®, up to 5 mm above the upper face (which in the case of treated samples was the consolidated face), with the double goal of inducing a unidirectional flow of the saline solution and collecting efflorescence and fragments detached from the samples during the cycles. Then, the samples were contaminated with salt, by making them absorb by capillarity, through the face opposite to the consolidated one, a certain amount of a 5 wt% aqueous solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The amount of saline solution to be absorbed by each sample was fixed as equal to the capillary moisture content (CMC) of the material [36]. For the lime mortars used in this study, the CMC was assessed as 3.8 kg/m^2 by preliminary tests on 3 replicates. Then, the lower surface of the samples was sealed with Parafilm® and adhesive tape and the contaminated samples were dried at 40°C , until evaporation of 80% of the absorbed solution [36]. Once reached this condition, the “accumulation phase” was concluded and the “propagation phase” started, which consisted in cycles of solubilization and crystallization of the salts initially introduced into the samples. Each cycle consisted in making the samples absorb a certain amount of deionized water (not saline solution, like in the EN standard). An amount of water corresponding to 80% of the initial weight of the saline solution was introduced into the samples by capillarity from the lower surface. After re-applying the Parafilm®, the samples were dried in room conditions for 24 h and then in oven at 40°C for 13 days. Afterwards, the samples were cooled to room temperature for 4 h, then the Parafilm® was removed from the bottom of the sample [36] and also the lateral surface (as preliminary tests indicated that this caused no significant material loss). In total, 10 propagation cycles were performed, to equal the number of “EN cycles”.

It should be noted that, in the present study, the EN cycles and the RILEM cycles were performed to assess the durability of lime mortars, although the respective tests had been developed on different types of materials, namely natural stones with open porosity greater than 5% for the EN cycles [28] and natural stones and fired bricks with open porosity in the range 13–50% [36]. Also the size of the specimens used in this study ($30 \times 30 \times 20 \text{ mm}^3$) was different from what prescribed by the European Standard [28] (40 mm cubes) and the RILEM Recommendation



[36] (cylinders with 50 mm diameter and 50 mm height).

2.4 Sample characterization

2.4.1 Preliminary desalination

In the case of samples subjected to the salt weathering, at the end of the cycles the samples were desalinated, to evaluate the changes in weight, pore size distribution and mechanical properties without salts interference. The entire external surface of each sample was wrapped with a poultice of cellulose pulp and deionized water (1:4 w/w), then samples were wrapped with plastic film for 24 h. Afterwards, the samples were unwrapped and left to dry at room temperature while still covered with the poultice, so that the saline solution was progressively transported from the sample to the poultice, where salts finally crystallized. To ensure complete removal of the salts, the desalination process was performed twice.

2.4.2 Ion chromatography

After desalination following the “EN cycles” and “RILEM cycles”, ion chromatography was performed to determine the amount of salt remaining in the samples. The salt extraction from the samples was performed following the indications of the European Standard EN 772–5 [53]. Fragments of samples that had been subjected to mechanical tests (see below) were crushed and immersed in plastic containers containing bi-distilled water (20 g of sample in 200 ml of water). After 24 h of salt extraction by keeping the containers in rotatory motion (150 rpm) at room temperature, the suspensions were filtered, and the solutions analyzed by a Dionex ICS 1000 Ion Chromatography System. Duplicate samples were tested for each condition.

2.4.3 Dynamic elastic modulus (E_d)

Taking advantage of the non-destructive nature of the test and its correlation with the mechanical properties of the material [54], E_d was determined before and after consolidation and then after each ageing cycle. E_d was calculated according to the formula $E_d = \rho \times UPV^2$, where ρ is the density and UPV is the ultrasonic pulse velocity across the samples,

measured by using a Pundit instrument with 55 kHz transducers. The UPV and hence the E_d were determined in two orthogonal directions, namely parallel and perpendicular to the 30×30 mm² face. As pointed out in previous studies [24, 55], by comparing changes in E_d measured in different directions one can obtain qualitative information on the penetration depth of consolidants and/or on damage induced by salt crystallization. In fact, in the case of consolidation, E_d measured parallel to the consolidated surface is not significantly influenced by the thickness of the consolidated layer, while E_d measured in the perpendicular direction is strongly reduced in case of scarce consolidant penetration, because in this case the ultrasonic pulse has to cross the whole sample thickness, so the presence of any unconsolidated, slower layer is detected. Similarly, in the case of salt weathering, E_d measured parallel to the surface through which evaporation of the saline solution takes place is little affected by possible surface delamination, while E_d measured in the perpendicular direction is significantly reduced by formation of cracks parallel to the evaporation surface.

2.4.4 Compressive strength by double punch test (DPT)

Originally proposed for the mechanical characterization of mortar samples obtained from historic masonries [56], the DPT was here adopted as it allows to reliably test small specimens like those used in this study. The mortar samples were loaded in the center of the 30×30 mm² face by using steel platens with 20 mm diameter (the platen size being selected to match the specimen thickness, according to previous results [57]). The compressive test was performed using a Galdabini testing machine, adopting a speed of 3 daN/sec and a maximum load of 500 daN. The resulting compressive strength was calculated as the ratio of the failure load to the loaded area.

2.4.5 Mercury intrusion porosimetry (MIP)

Alterations in open porosity and pore size distribution induced by the consolidants and by the ageing cycles were assessed by MIP, using a 140 and 240 Pascal instrument (minimum pressure 0.0125 MPa, maximum pressure 200 MPa). The MIP samples were fragments of mortar specimens that had been

subjected to the DPT (which in turn was performed after desalination of the samples subjected to the salt weathering cycles). To ensure the representativeness and the reliability of the measurements, all the samples had comparable size (roughly cubes with 8 mm side) and, in case of consolidated samples, included the treated surface. Duplicate samples were tested for each condition.

3 Results and Discussion

3.1 Effects of the ageing cycles on non-consolidated mortar

As shown in Fig. 1, the three accelerated ageing procedures had significantly different effects on lime mortar specimens not previously subjected to consolidation. This is also evidenced by the appearance of the specimens at the end of the cycles, compared to the initial condition, as illustrated in Fig. 2.

The “FT cycles” caused progressive material loss, linked to a progressive reduction in E_d registered in both directions. While material loss started to be dramatic from the 5th cycle, $E_{d//}$ and $E_{d\perp}$ already showed significant decreases after the 1st cycle. This is an indication that cracks started to form from the 1st cycle and then propagated, even though detachment of fragments and pulverization started to be dramatic from the 5th cycle. After 7 cycles, the material loss was so pronounced that the samples had lost their regular shape (Fig. 2) and the E_d measurement had become very challenging. At the end of the cycles, the samples suffered a dramatic weight loss and a reduction in compressive strength, which passed from 3.2 to 0.7 MPa.

MIP performed on samples collected at the end of the “FT cycles” revealed an increase in open porosity, mostly due to an increase in pores with diameter $\sim 0.5 \mu\text{m}$ (Fig. 3), which may be ascribable to the formation of new cracks due to the freezing–thawing cycles.

The salt weathering cycles induced different effects depending on the adopted procedure. In the case of the “EN cycles”, an initial increase in E_d in both directions was registered, as a result of the progressive filling of pores by salts introduced with each cycle. Accordingly, the sample weight

initially increased due to salt accumulation. After the 7th cycle, the $E_{d\perp}$ started to decrease, indicating that crack formation and delamination had started to severely affect the cohesion of the mortars. At the end of the 10 cycles and after desalination, the samples exhibited an average decrease in weight by 6% and decrease in compressive strength by 32% (Fig. 1). It is noteworthy that, after desalination, $E_{d\perp}$ exhibited an apparent *increase*, which can be explained considering that salt removal from the cracks allowed partial closure of the cracks and reestablishing a better continuity in the mortar sample. Formation of new cracks after the “EN cycles” is evidenced by the increase in the volume of pores with diameter $\sim 0.5 \mu\text{m}$ revealed by MIP (Fig. 3).

In the case of the “RILEM cycles”, the weight increased at the beginning of the cycles and the changes in E_d in the two directions were much less pronounced than in the case of the “EN cycles” (Fig. 1). This is a consequence of the different concentration of the salt solution introduced in the first cycle in the two cases (14 wt% for the “EN cycles”, 5 wt% for the “RILEM cycles”) and the different contamination conditions adopted in the following cycles (again 14 wt% salt solution for the “EN” cycles, only water for the “RILEM cycles”) [28, 36]. These differences are also in line with the sensibly different amounts of soluble salts found in the two types of samples at the end of the test (after desalination), namely 0.54 wt% for the “EN cycles” and 0.02 wt% for the “RILEM cycles” (Fig. 4). At the end of the “RILEM cycles”, a modest decrease in weight by 1% (Fig. 1) and a minor alteration in pore size distribution (Fig. 3) were registered, which are consistent with the little alteration of the sample appearance (Fig. 2). At the end of the cycles, an apparent decrease in compressive strength by 19% was also registered, which is however thought to be partly due to the relatively high scatter of compressive strength values before the cycles ($\sigma_c = 3.7 \pm 1.0 \text{ MPa}$ before the cycles vs $\sigma_c = 2.9 \pm 0.5 \text{ MPa}$ after the cycles).

Overall, the “FT cycles” appear to be the most aggressive ageing procedure among those tested in this study on lime mortars. Between the two salt weathering procedures, the “EN cycles” resulted more aggressive than the “RILEM cycles” both in terms of E_d and σ_c , as expected.



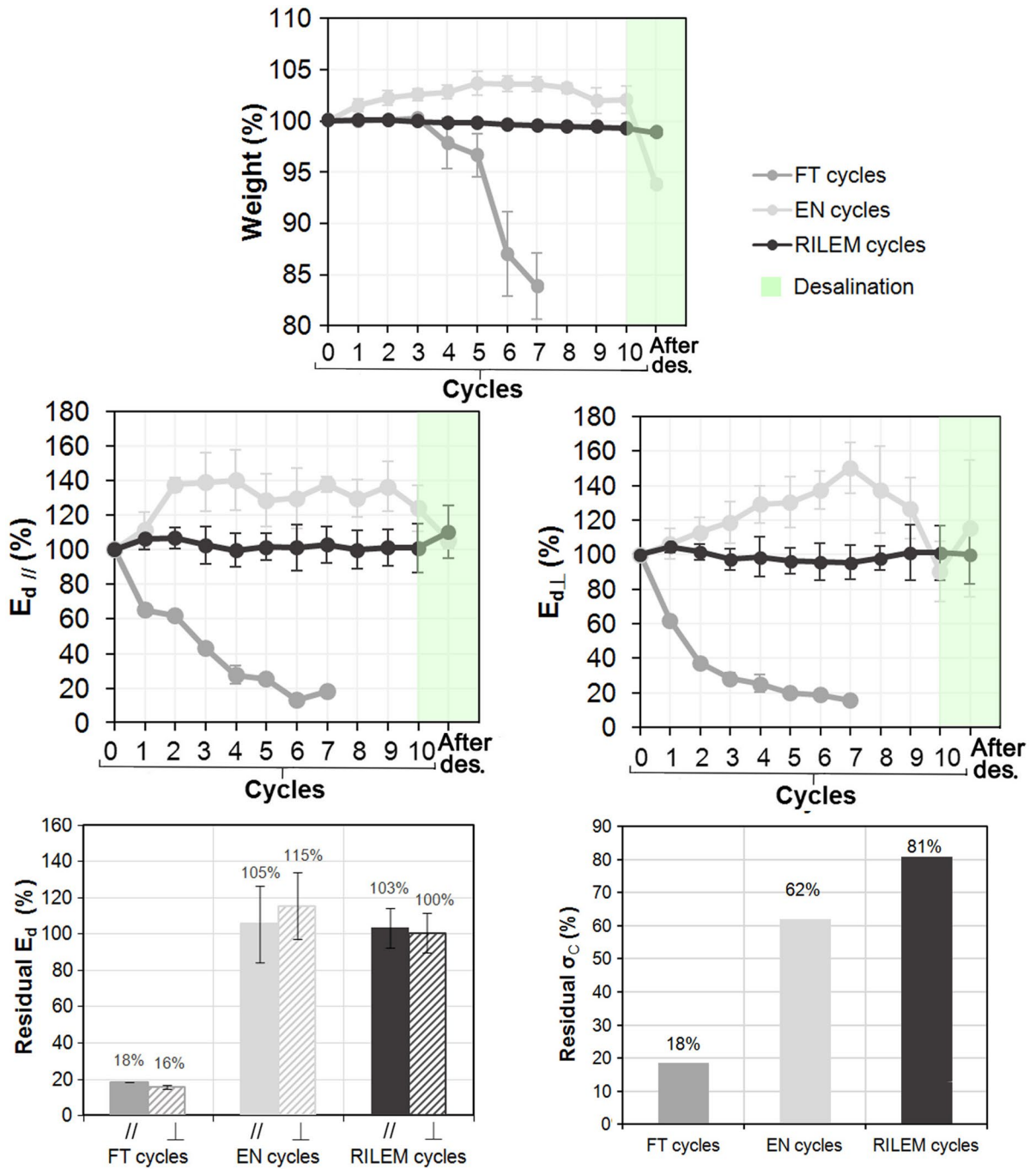
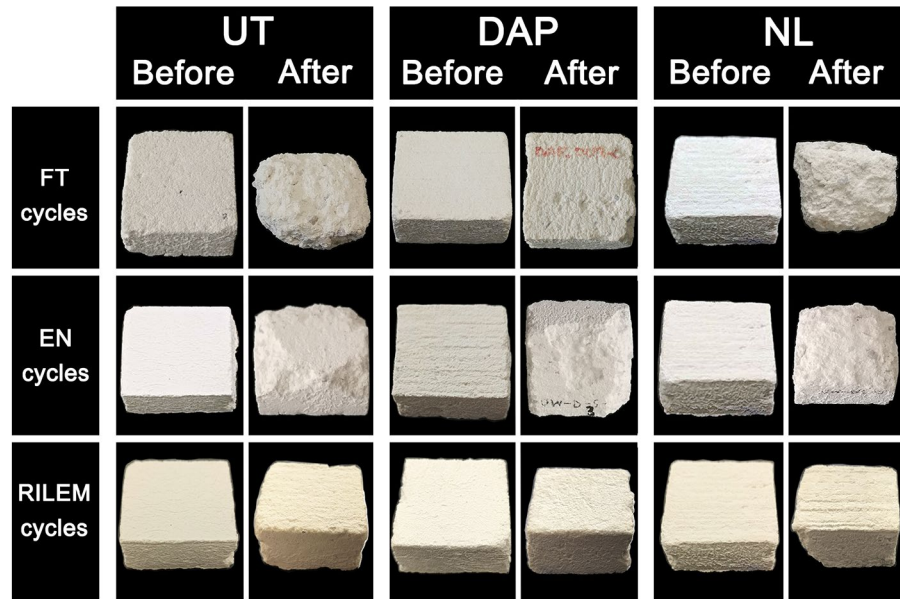


Fig. 1 Percentage variations in weight (top) and E_d (middle) as a function of the number of cycles and final percentage variations in E_d and σ_c (bottom) of untreated samples subjected to “FT cycles”, “EN cycles” and “RILEM cycles”, with respect to the condition before the cycles. In the case of the FT cycles, the residual E_d was evaluated after 7 cycles (instead of 10

cycles, like for the other two ageing procedures), as the “FT cycles” were then stopped because the samples were severely damaged. In the case of the “EN cycles” and “RILEM cycles”, after the 10th cycle the samples were desalinated (as indicated by the green shade) and then the measurements were repeated

Fig. 2 Appearance of the samples before and after being subjected to accelerated aging by the three methods



3.2 Effects of the consolidating treatments

The brush application of the two consolidants led to product uptakes of $4.1 \pm 0.7 \text{ kg/m}^2$ for DAP and with $2.3 \pm 0.8 \text{ kg/m}^2$ for NL (Table 2), in agreement with values reported in previous studies [24, 27]. The significant difference between the two treatments can be explained considering the different concentration of the two products (Table 2), namely 396 g/L for DAP (using water as solvent) and 5 g/L for NL (using ethanol as solvent).

After hardening, the new consolidating phases formed in the two cases (calcium phosphates for DAP, calcium carbonate for NL) led to the increases in mechanical properties reported in Fig. 5.

While the DAP treatment caused significant increases in E_d in both directions and in compressive strength (although σ_c values showed high dispersion), the NL treatment did not provide any significant benefit compared to the untreated condition (error bars completely overlap). This trend is in line with previous results obtained on mortars [24, 26], as well as on carbonate stones [58]. By comparing E_d values registered in the two directions, for all conditions $E_{d//}$ was slightly higher than $E_{d\perp}$ (Fig. 5), but with significant overlap of the error bars. Previous studies have proposed that differences in the increase in E_d registered in different directions may be used to derive

some qualitative information on the penetration depth of consolidants [55], but in the present case the differences are minimal. Moreover, a difference between the two directions is present also in the untreated reference, which suggests that these small differences are most likely due to some anisotropy owing to the mortar preparation.

The new consolidating phases were responsible for the alterations in pore size distribution and water absorption shown in Fig. 6. While NL caused only minor changes, the DAP-treatment led to a shift of the pore size distribution towards smaller pores, as a result of the partial filling of bigger pores, in agreement with previous findings on porous limestone [21, 49] and mortar [27]. Notwithstanding this slight alteration in the pore system, also in the case of DAP, the water sorptivity and the final water absorption at the end of the test were basically unchanged (Fig. 6).

In terms of possible risks of “delayed incompatibility” due to the produced changes in pores size distribution, smaller pores are known to experience higher crystallization pressure [9] but, in turn, they absorb water more slowly than bigger pores [8], so they can be less water-accessible. Moreover, in the case of freezing, the presence of bigger pores ($\sim 10 \mu\text{m}$ diameter) in the studied mortars may mitigate damage, because ice crystals growth is energetically more favorable in larger pores, which can hence drain the water from the smaller

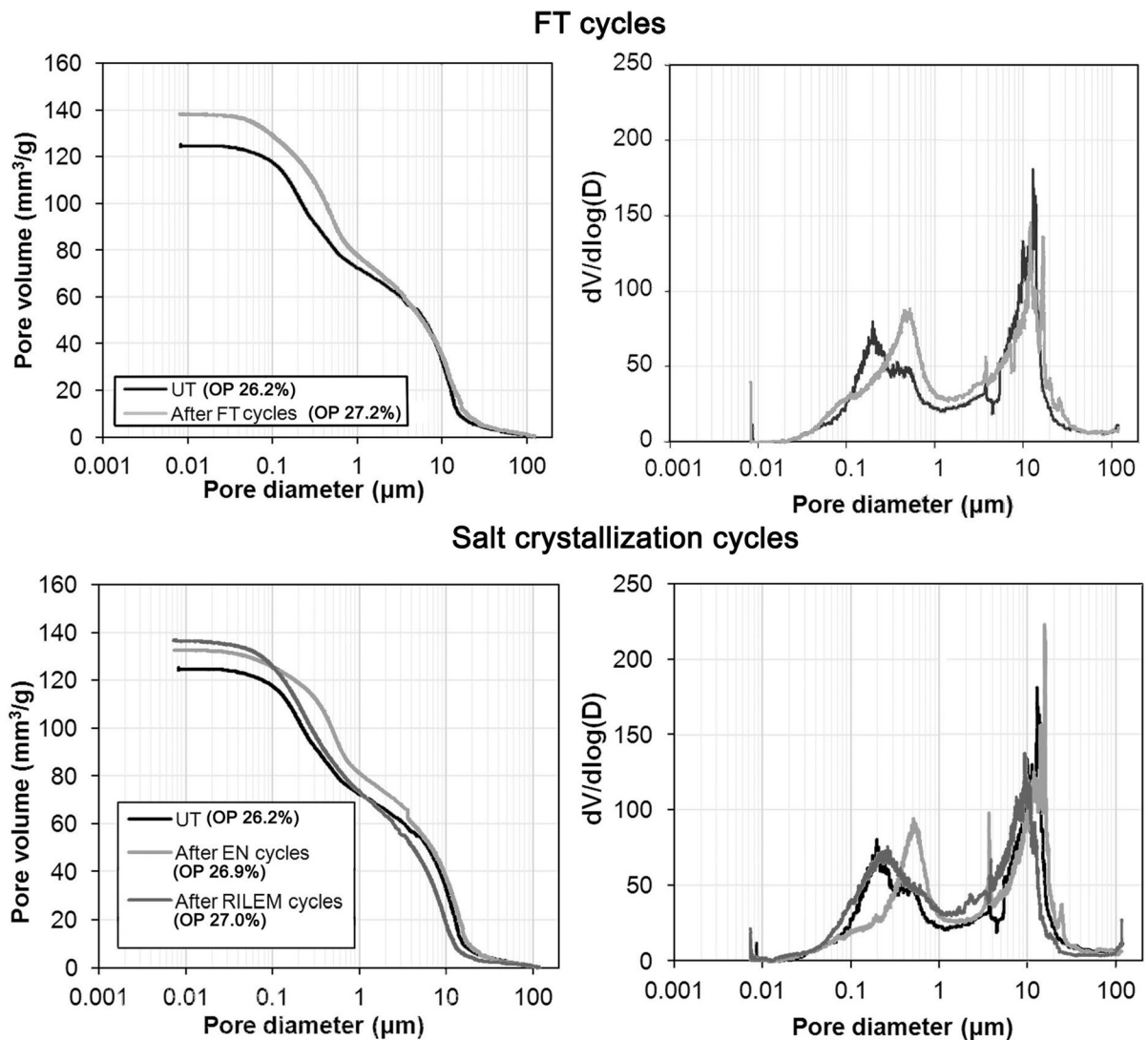


Fig. 3 Variations in the pore size distribution of untreated samples after being subjected to “FT cycles”, “EN cycles” and “RILEM cycles” (OP=open porosity)

pores upon freezing [59]. Also considering that the new binding phases are expected to increase the mortar tensile strength, it is difficult to predict whether the changes in pore size distribution caused by the consolidating treatments will result in increased susceptibility to freezing–thawing and salt crystallization cycles, hence experimental tests were carried out, as described in the following.

3.3 Effects of the ageing cycles on consolidated mortars

3.3.1 Freeze–thaw cycles

When mortar samples consolidated by DAP and NL were subjected to accelerated ageing by the “FT cycles”, the results reported in Fig. 7 were obtained.

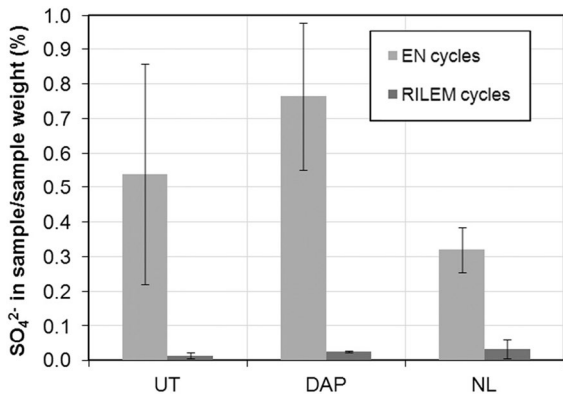


Fig. 4 Amount of soluble salts detected, after desalination, at the end of the salt weathering test by the “EN cycles” and “RILEM cycles”

While untreated samples and, to a lower extent, NL-treated samples exhibited significant decreases in $E_{d//}$ and $E_{d\perp}$ already during the first cycle, in the case of DAP-treated samples the level of deterioration was significantly lower. Accordingly, the specimens suffered from dramatic weight loss starting from the 5th

cycle for the UT samples and from the 7th cycle for the NL ones, while the DAP-treatment was the only one able to prevent material loss and detachments until the end of the test (10 cycles). As a result, when compressive strength was assessed at the end of the test, the residual σ_c amounted to only 18% for UT and 41% for NL, while for DAP-treated samples the residual σ_c was still 72%.

Compared to the condition right after consolidation (Fig. 6), the pore size distribution of the samples subjected to the “FT cycles” underwent some modification. In the case of the NL-treatment, a shift of the pore size towards smaller pores was detected, while in the case of DAP there was an increase in the amount of pores with diameter around 5 μm , so that the final pore size distribution of the DAP samples approached those of the UT and NL samples.

Even though the DAP treatment was responsible for a shift of the pore size distribution towards smaller pores, which may be potentially negative as ice crystallization pressure is higher in smaller pores, still the resistance to FT cycles was higher for the DAP-treated samples than for the other conditions

Table 2 Concentrations values of the of the consolidants and their amounts in the samples

Consolidant	Product concentration	Application method	Product uptake (kg/m ²)
NL	5 g/L (ethanol as solvent)	Brushing until apparent refusal	2.3 ± 0.8
DAP	396 g/L (water as solvent)	Brushing until apparent refusal	4.1 ± 0.7

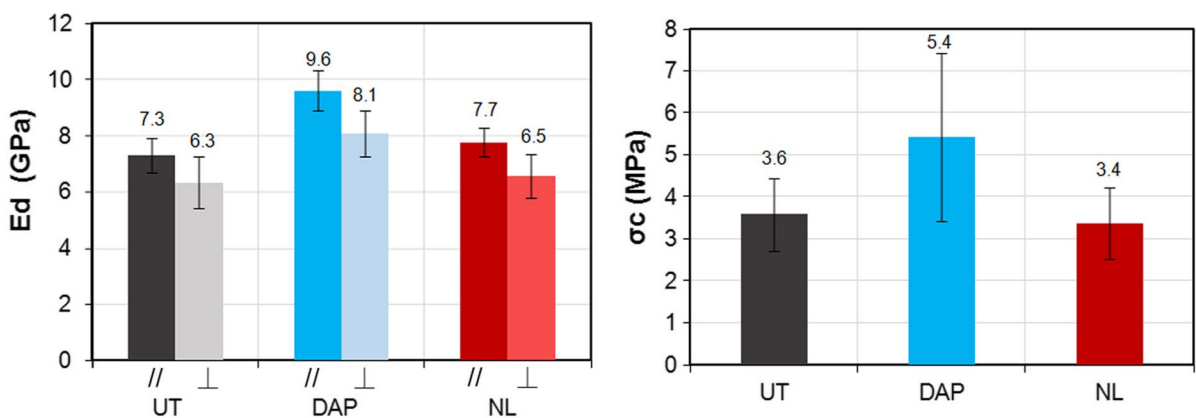


Fig. 5 Values of dynamic elastic modulus (E_d , left) and compressive strength (σ_c , right) of untreated and consolidated specimens (values are averages for 3 samples, error bars indicate standard deviation)



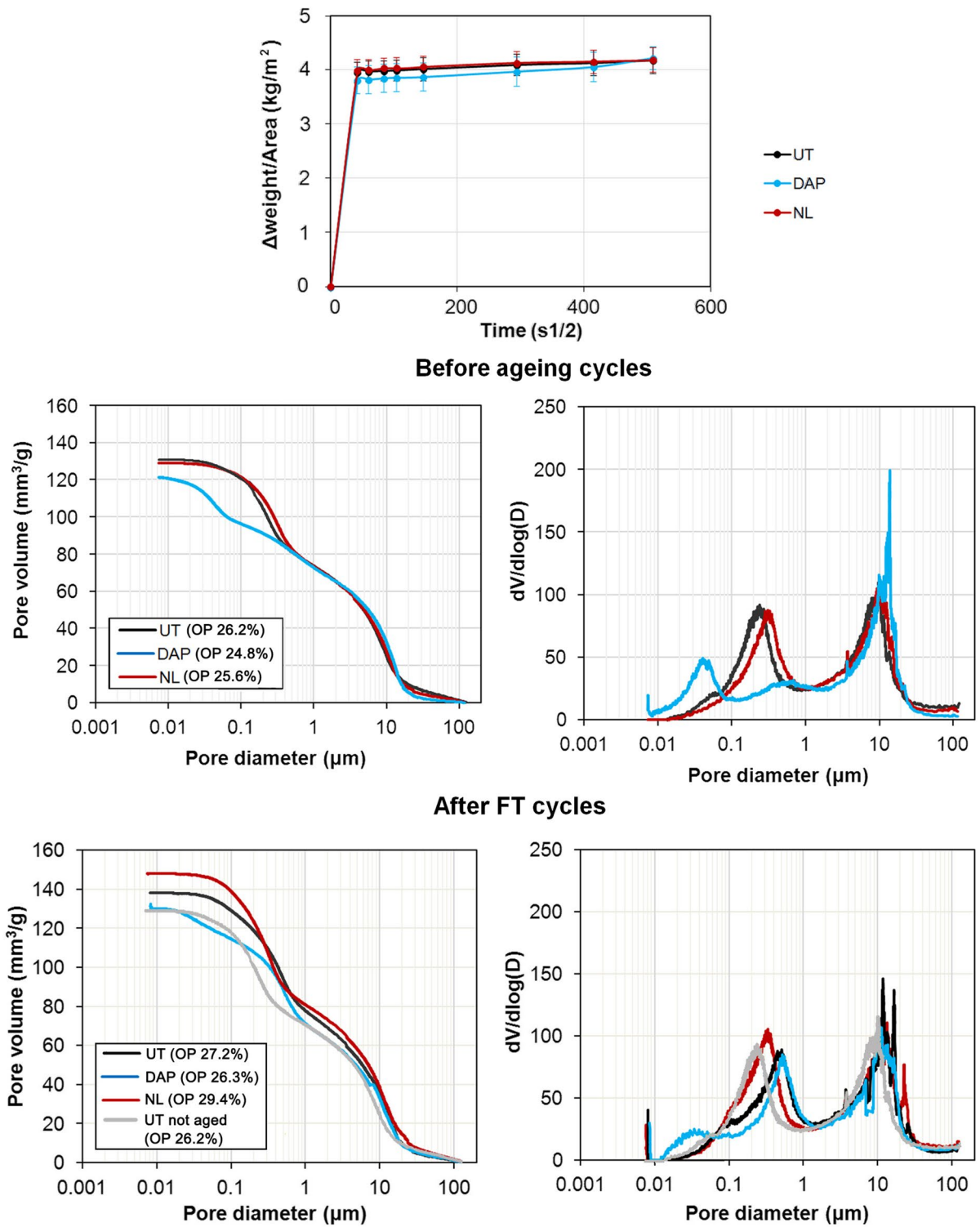


Fig. 6 Water absorption (top) and pore size distribution of untreated and consolidated samples right after consolidation (medium) and after the FT ageing cycles (bottom) (OP= open porosity)

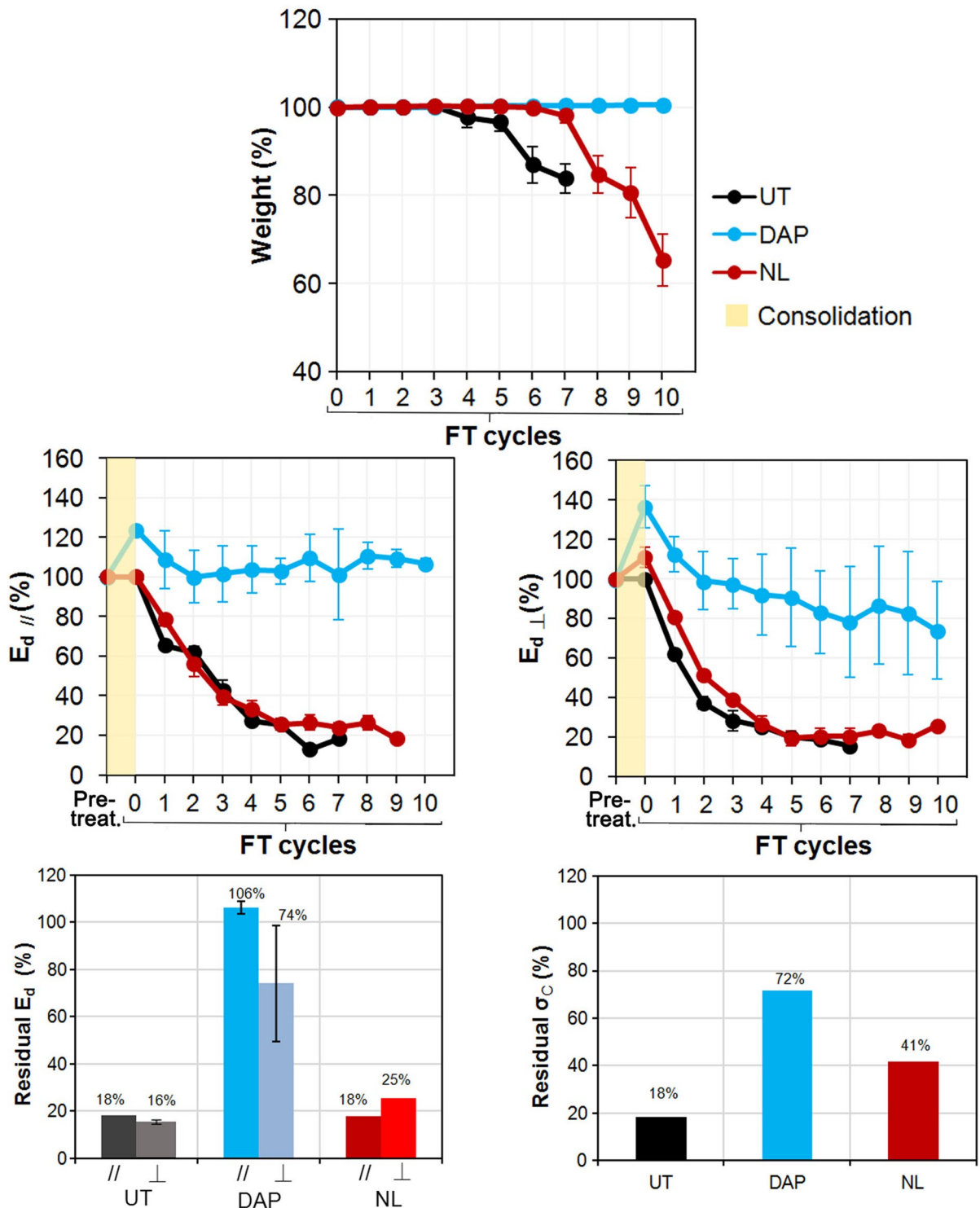


Fig. 7 Percentage variations in weight and E_d as a function of the number of cycles (top) and variations in E_d and σ_c (bottom) of untreated and consolidated samples subjected to the “FT cycles”. In the case of E_d , the initial value of 100% cor-

responds to the condition before consolidation, which is indicated by the yellow shade. At the cycle 0 (i.e. after consolidation and before the ageing cycles started), E_d values higher than 100% are the effects of the consolidant application



(Fig. 7). Considering that the water sorptivity was substantially unaltered by the treatment (Fig. 6), it is likely that the smaller pores formed by the DAP treatment were filled with water that underwent freezing, but the increase in mechanical properties induced by the treatment was able to compensate the increase in crystallization pressure experienced in smaller pores upon freezing.

3.3.2 Salt crystallization cycles

The effects of accelerated ageing by salt weathering cycles performed according to the EN procedure and the RILEM procedure are reported in Fig. 8.

The “EN cycles”, which involved a more concentrated saline solution than the “RILEM cycles”, caused higher increases in weight and in E_d at the beginning of the test, owing to more significant pore occlusion. In fact, the ultrasonic wave travels faster in pores filled with salt rather than in empty ones. Therefore, at the beginning of the test the salts presence led to an apparent increase in the elastic modulus; then, as the cycles progressed, the degradation caused by salts crystallization became predominant and E_d started to decrease [60, 61].

Among the three conditions, the DAP samples exhibited higher E_d values than the UT references and the NL samples for the first 6 cycles. Then, during the 7th cycle, the DAP samples experienced a marked weight loss and decrease in $E_{d\perp}$, while $E_{d//}$ did not show such a drop. This is thought to be a consequence of crack formation parallel to the treated surface and hence detected in terms of $E_{d\perp}$ (measured perpendicular to the treated surface) but not in terms of $E_{d//}$ (as in this direction the ultrasonic pulse travels through the densest path available). The salt-induced formation of cracks parallel to the treated surface is also suggested by the fact that, when the samples were desalinated at the end of the cycles, an actual *increase* in $E_{d\perp}$ was registered, because salt removal from the cracks allowed “re-compacting” the mortar layers. Differently, in the parallel direction desalination did not cause such “compaction”, but, on the contrary, it induced a slight decrease in $E_{d//}$ as the pores were emptied from the salts. Such a different effect of desalination in the two directions (increase in $E_{d\perp}$ and decrease in $E_{d//}$) was similar for all the three conditions, suggesting that salt removal caused

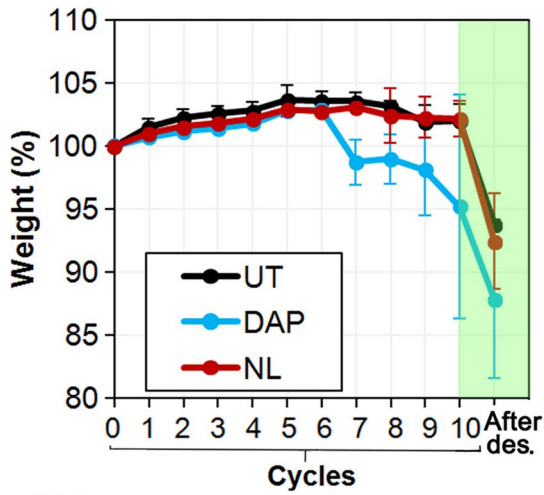
crack closure and mortar layer “compaction” also in the NL and UT samples (Fig. 8).

Formation of cracks parallel to the treated surface, with possible delamination of a surface layer, may be a sign of “delayed incompatibility” caused by the formation of a harder, denser layer near the treated surface. The possible formation of such a hard crust was specifically investigated in a previous study [26] where lime-based mortars were treated with DAP. In that case, no clear evidence of formation of a surface crust was detected by SEM observation [26], but complementary techniques would be needed to conclusively assess the gradient in properties with depth.

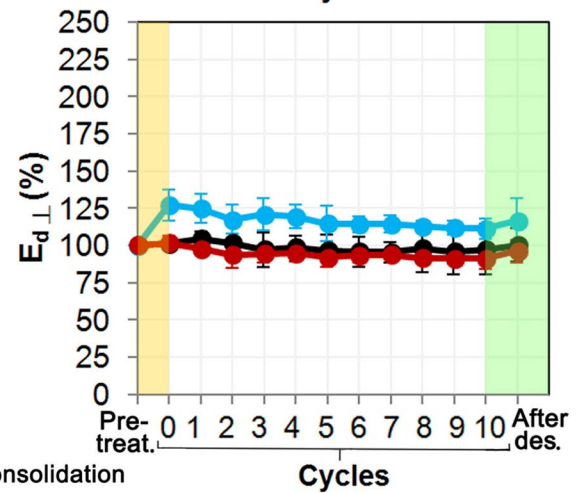
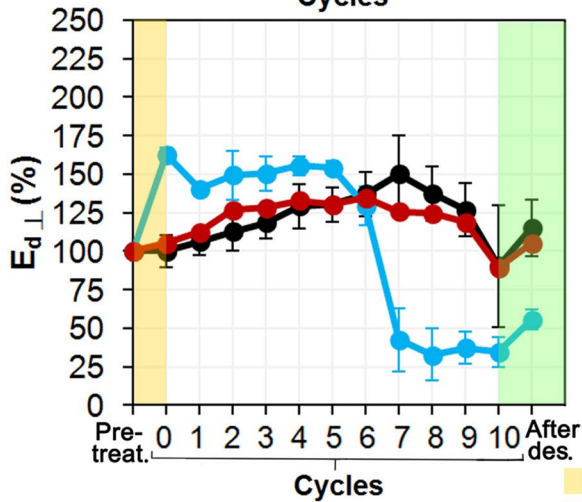
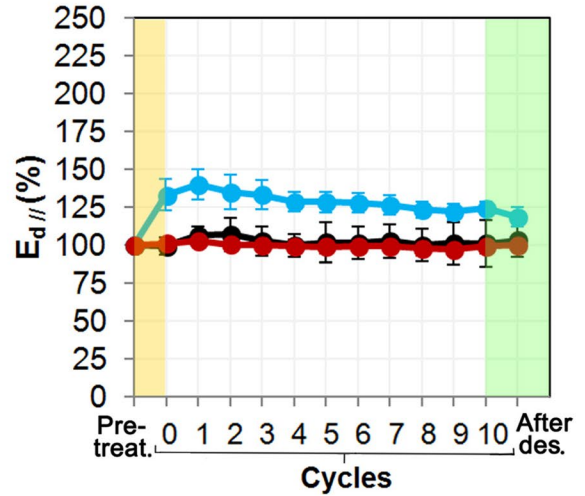
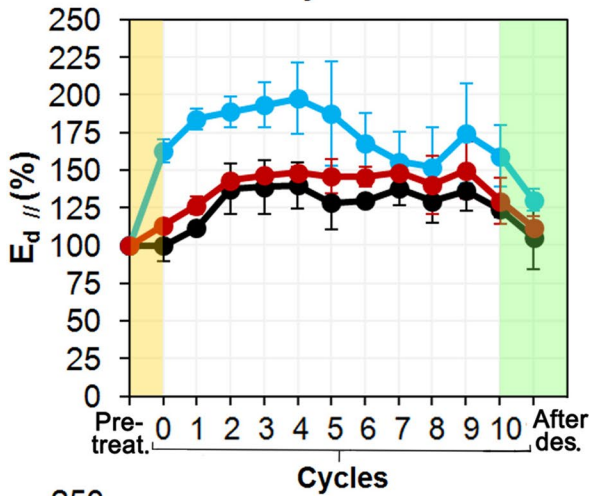
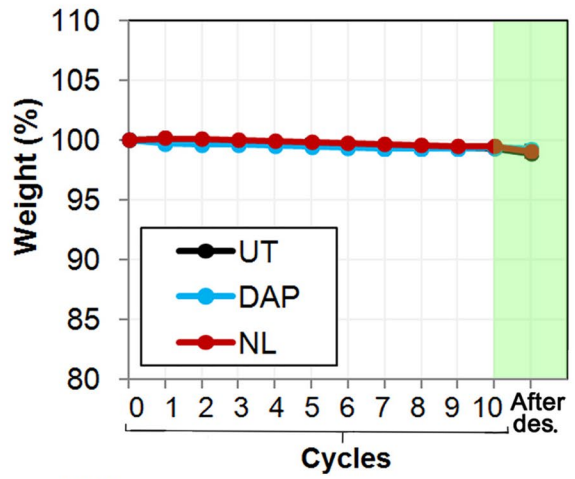
At the end of the 10 “EN cycles”, destructive mechanical testing was performed, to assess differences between the various conditions (Fig. 9). Taking the compressive strength of the untreated mortar as reference, after the “EN cycles” the UT samples exhibited a residual compressive strength of 62%, which indicates that the cycles induced significant damage, as expected. In fact, the σ_c of the untreated samples decreased from 3.6 ± 0.9 MPa before the cycles to 2.2 ± 0.4 MPa after the cycles. Compared to the untreated reference, the residual compressive strength of the consolidated specimens was higher for the NL samples (2.9 ± 0.2 MPa, 82% of the initial UT value) and especially for the DAP samples (3.6 ± 0.9 MPa, 100% of the initial UT value). This indicates that, even though the DAP samples experienced deterioration during the cycles (after consolidation, before the cycles, the DAP samples showed σ_c equal to 5.4 ± 2.0 MPa, Fig. 5), still at the end of the cycles the DAP treatment was able to guarantee a residual compressive strength equal to that of the mortar before consolidation and before ageing.

In the case of the “RILEM cycles”, which involved initial contamination with a less concentrated saline solution than the “EN cycles” and subsequent cycles of impregnation with water (not saline solution), the increase in E_d at the beginning of the test and the progressive E_d decrease as the cycles progressed were much less pronounced than in the case of the “EN cycles” (Fig. 8). Accordingly, the sample weight remained practically constant for the whole duration of the test. Among the three conditions, the DAP-treated samples always exhibited the highest E_d during the 10 cycles, E_d values higher than 100% being the effect of consolidation ($E_d = 100\%$ corresponds to the initial condition before consolidation). At the end

EN cycles



RILEM cycles



Consolidation
Desalination



◀**Fig. 8** Percentage variations in weight and E_d as a function of the number of cycles of untreated and consolidated samples subjected to the “EN cycles” (left) and the “RILEM cycles” (right). In the case of E_d , the initial value of 100% corresponds to the condition before consolidation, which is indicated by the yellow shade. At the cycle 0 (i.e. after consolidation and before the ageing cycles started), E_d values higher than 100% are the effects of the consolidant application. After the 10th cycle, the samples were desalinated (as indicated by the green shade) and the measurements were repeated

of the test, when the residual compressive strength was assessed, the UT showed a residual σ_c of 81% (σ_c decreased from 3.6 ± 0.9 MPa to 2.9 ± 0.5 MPa). This shows that salt-induced damage occurred but to a lower extent than in the case of the “EN cycles”, for which σ_c of the UT samples decreased to 62% of the initial value (Fig. 9). In the case of NL, the residual σ_c was similar to the UT reference (2.9 ± 0.4 MPa, 80% of the initial UT value). In the case of DAP, notwithstanding some degradation caused by the cycles, the residual σ_c was much higher than in the other cases (6.0 ± 1.4 MPa, 168% of the initial UT value), thus indicating that a substantial benefit was still present at the end of the cycles. The improvement in mechanical properties due to consolidation was higher than the salt-induced damage, to an even higher extent than in the case of the “EN cycles” (Fig. 9). The apparent discrepancy registered for DAP samples between the σ_c right after consolidation (+150% compared to the unaged UT reference) and the residual σ_c after the “RILEM cycles” (+168% compared to the unaged UT reference) is due to the scatter of σ_c results obtained in the two cases (5.4 ± 2.0 MPa vs 6.0 ± 1.4 MPa, respectively). This, in turn, is due to the fact that, unlike the case of E_d , σ_c measurement is a destructive test, which had to be performed on different samples (in other words, the comparison is between unconsolidated and consolidated samples, and not between the same samples before and after consolidation). However, considering the overlapping of the error bars, the apparent improvement in σ_c after the “EN cycles” can actually be considered as a substantial maintenance of the initial properties.

In terms of pore size distribution, there was no case in which dramatic alterations were detected in the untreated and consolidated samples after neither the “EN cycles” nor the “RILEM cycles” (Fig. 10). In the case of the “EN cycles”, some pore occlusion was registered, especially for the DAP samples,

which is in agreement with the presence of residual sulfates detected in the samples even after desalination (Fig. 3).

4 Conclusions

In the present study, untreated and consolidated lime mortars were subjected to accelerated ageing cycles, to assess their durability after impregnation with a diammonium hydrogen phosphate aqueous solution (DAP treatment) and with a dispersion of nanolimes (NL treatment). Durability was assessed in terms of resistance to accelerated ageing by freeze–thaw cycles (performed by partly modifying the European standard EN 12371 [37]) and salt crystallization cycles, performed according to the European standard EN 12370 [28] and to the procedure recently proposed by the RILEM TC 271-ASC [36].

Based on the findings of the present paper, the following conclusions can be derived:

- Among the three ageing procedures, the freeze–thaw cycles resulted the most aggressive one, the rate of decrease in weight and dynamic elastic modulus being higher than in the case of both salt weathering procedures and the residual compressive strength at the end of the cycles being lower.
- Between the two salt weathering procedures, the “EN cycles” resulted more aggressive than the “RILEM cycles”, as expected, as they induced higher losses in weight, dynamic elastic modulus and compressive strength. For the untreated mortar, the weight loss at the end of the cycles amounted to 6% for the “EN cycles” and 1% for the “RILEM cycles”, while the residual compressive strength was 62% after the “EN cycles” and 81% after the “RILEM cycles”. This is a consequence of the fact that the “EN cycles” involve repeated saturation with a highly concentrated solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, while the “RILEM cycles” involve a first phase of salt accumulation (by impregnation with a less concentrated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ solution) and then a phase of damage propagation (produced by repeated cycles of wetting with water and drying).
- In terms of performance of the two consolidants, the DAP-based treatment was able to significantly reduce damage in the case of the freeze–

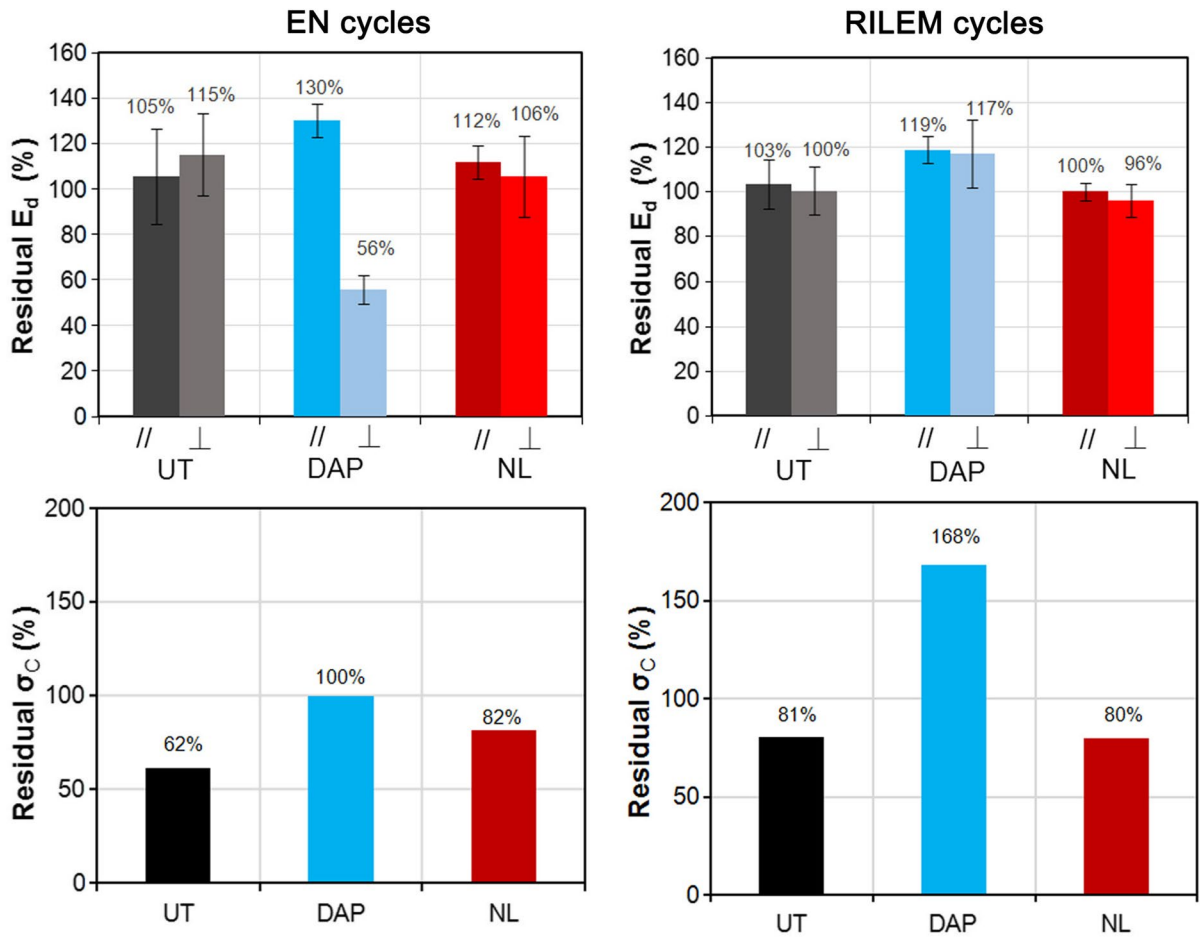


Fig. 9 Variations in E_d (top) and σ_c (bottom) of untreated and consolidated samples subjected to “EN cycles” (left) and “RILEM cycles” (right), after desalination. For both E_d and σ_c , the untreated mortar before consolidation and ageing was taken as reference, hence residual values higher than 100% indicate

that a benefit is still present at the end of the cycles (in the case of E_d , some influence from residual salts in the pores even after desalination likely also contributes to the registered residual values)

thaw cycles and the “RILEM cycles” (DAP samples basically experienced no weight loss and exhibited residual compressive strength sensibly higher than the untreated reference). In the case of the “EN cycles”, the DAP samples exhibited a sudden decrease in $E_{d\perp}$ and a corresponding weight loss, likely due to the formation of cracks parallel to the treated surface and some detachment. This may be a sign of the formation of a surface layer with different properties, which may lead to “delayed incompatibility” in the medium-long term, even though in no previous study was the formation of a hard surface crust clearly assessed after the DAP treatment.

Nonetheless, at the end of the cycles, the DAP-treated samples exhibited a residual compressive strength comparable to that of the untreated reference before the cycles, thus indicating that benefits deriving from the application of the consolidant were still present. Overall, considering that, on the one hand, the residual compressive strength of DAP samples was significantly higher than that of the other conditions but also considering that, on the other hand, compressive tests have relatively little sensitivity to the presence of cracks perpendicular to the loading direction, further testing is recommended to ascertain the presence and extent of cracks paral-

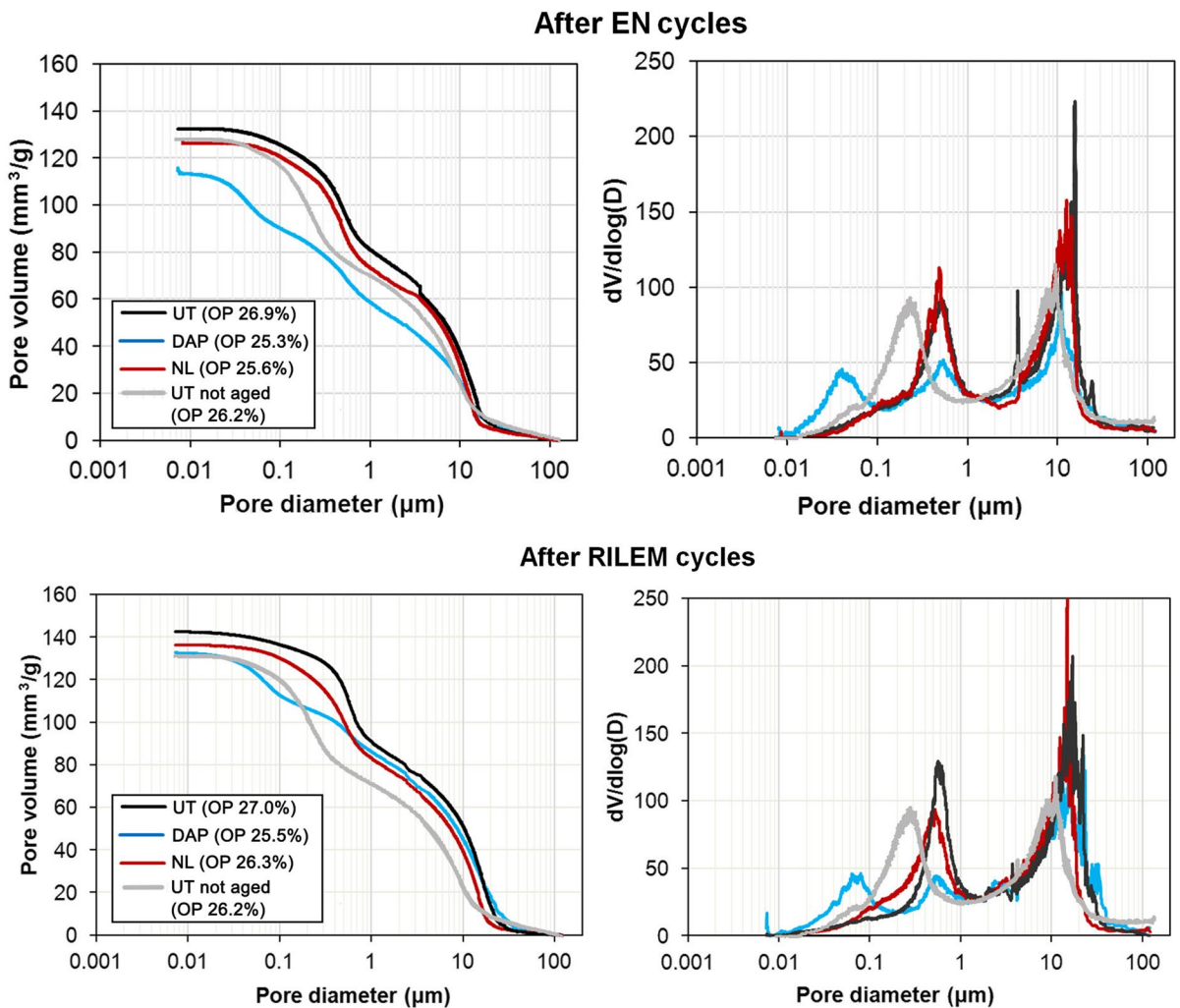


Fig. 10 Pore size distribution of untreated and consolidated samples right after consolidation (top) and after the ageing cycles by the two salt crystallization methods (OP=open porosity)

lel to the treated surface, which may lead to surface delamination.

- Differently from the DAP treatment, the NL treatment did not provide significant improvements neither right after the consolidant application nor during the ageing cycles, so the performance of the NL samples was substantially similar to that of the untreated ones.

Overall, the present study confirmed the expected difference in the aggressiveness of the EN and RILEM procedures. The EN procedure highlighted some possible risk of “delayed incompatibility” caused by the DAP treatment, which was

not evidenced by the RILEM procedure. However, the actual reliability of such “delayed incompatibility” risk needs to be further elucidated in future research, considering the known limits of the EN procedure, and considering that no such risk was evidenced by the freeze–thaw cycles. In other words, the risk highlighted by the EN procedure in the case of the DAP treatment is an outcome of the combination between the salt weathering procedure itself and the consolidating treatment. It should be finally noted that, between the two sodium sulfate concentrations recommended in the RILEM recommendation (5 wt% and 10 wt% [36]), only the less concentrated one was tested in this study, hence

future tests adopting the more concentrated solution are also recommended to obtain a more complete picture.

Funding Open access funding provided by Alma Mater Studiorum - Università di Bologna within the CRUI-CARE Agreement.

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