RILEM Technical Letters (2024) 9: 76-86
https://doi.org/10.21809/rilemtechlett.2024.206

Consolidants in Salt-Weathered Masonry: Retention and Efficiency of DAP and TEOS

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Received: 26 November 2024 / Accepted: 07 January 2025 / Published online: 21 January 2025

Abstract

Consolidants are widely used to improve grain cohesion in monuments and sculptures under degradation. The porosity and pore size distribution of the substrate and the consolidant properties play a pivotal role in the efficient absorption and retention of the compounds. The substrate mineralogy is critical in product formation and essential for the substrates' long-term durability. In this study, the masonry components – brick, mortar and brick-mortar sandwiches – are consolidated by brushing with two different consolidants – phosphate-based DAP and silane-based TEOS. The accelerated salt weathering of specimens in chloride and sulphate solution simulated their deteriorated stage closer to reality before consolidation. The short-term and long-term effects of carbonation condition, pore size distribution, mineralogy and hygric resistance on the consolidation are investigated through microstructural analysis. The results highlight the importance of pore size distribution and porosity in the initial consolidant uptake and the significance of the compositional similarity between the substrate and the consolidant in the long-term retention amount of the consolidants. The observations indicate that TEOS consolidation's higher efficiency is at the expense of pore occlusion, which could adversely affect the systems' durability under salt weathering and freeze-thaw.

Keywords: Consolidation; Salt weathering; Diammonium hydrogen phosphate; Tetraethoxysilane; Masonry.

1 Introduction

Coastal masonry structures are susceptible to deterioration due to prolonged exposure to moisture, temperature fluctuations, wind and salt. The salt entering the porous building materials crystallizes upon reaching supersaturation within the pores. The nucleation and growth of these crystals exert stress on the pore walls and generate micro fissures, as the stress exceeds the tensile strength of the material. Consequently, this process, known as salt weathering, compromises material durability and adversely impacts masonry structures' functionality, appearance and integrity [1–6]. In addition to salt attack, continuous exposure to wind alters material properties and exacerbates material damage. The imparted damage, both physical and chemical in nature, affects the grain cohesion of materials, necessitating restoration efforts to maintain the material's original properties and prolong its service life [6–8].

Consolidants are fluids of small contact angle applied on the deteriorated material surface to reduce the progression of decay, arrest the decay, and improve grain cohesion and adhesion [5, 8–11]. Spraying, capillary suction, immersion, poulticing and brushing can be used to introduce consolidants to the substrates [5, 9, 10, 12–14]. They penetrate the porous materials, harden within the pores and improve the mechanical strength of the substrates [5]. The increase in the desired mechanical properties – the consolidation efficiency – depends on the amount of consolidant absorbed and the amount of product subsequently formed. Hence, material characteristics, such as porosity and pore size distribution, play pivotal roles along with the mode of application in ensuring consolidation efficiency and homogenous product distribution. Despite the low capillary suction potential, larger pores facilitate deeper consolidant penetration because of lesser frictional resistance, high surface tension, high sorptivity and low viscosity [5, 8, 9, 12]. In addition to the mode of application and the substrate characteristics, the consolidation efficiency also depends on consolidant characteristics, concentration and compatibility with the substrate [10, 13]. Compositional similarity is one of the critical parameters affecting consolidant compatibility with the substrate. Consolidants with a composition identical to substrate bond through chemical integration with the substrate. In contrast, those differing in composition bond physically with the substrate and can be further enhanced by coupling agents to improve adhesion [5, 15]. A deeper,

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homogenous penetration of the consolidants into the substrate is favourable for the effectiveness of consolidation [8]. The consolidants, typically less soluble than the substrate, are expected not to block the pores as they could alter the transport properties, ultimately aggravating frost and salt damage [5, 16]. Therefore, compatibility, durability, effectiveness, sustainability and reversibility/re-treatability are the major factors governing the selection of a consolidant [6, 9, 12, 17, 18]. Further research is necessitated to address the compatibility issues of consolidants with the substrates; the prevalent organic consolidants, such as epoxy and acrylic resins, are incompatible with the inorganic substrates. Globally used ethyl silicates also have compatibility issues with various substrates, especially carbonate-rich materials.

Alkoxysilanes, primarily ethyl silicates, have been widely used as a consolidant in silicate-rich substrates since the 1800s due to their low viscosity, ability to form Si-O-Si bond between the consolidant and the substrate, their thermal stability, resistance to discolouration, formation of harmless reaction products etc. [5, 14]. Consolidation by TEOS is obtained through hydrolysis of ethyl silicate forming silanol groups and further polycondensation of the silanol groups to form siloxane groups. They deposit as amorphous silica gel in the pores and connect the loose grains. However, they tend to crack during solvent evaporation and show poor efficiency on carbonate substrates due to their inability to form chemical bonds with carbonates [6, 9, 10, 14, 15, 17]. The residual ethoxy groups also keep the substrates hydrophobic for an extended period after consolidation and increase damage during salt crystallization and frost formation. In addition to these limitations, TEOS is observed to partly occlude the pores after consolidation, which could be preferred for the mechanical strength increment but could negatively alter the water and vapour transport properties, thus increasing the risk related to ice and salt crystallization [7, 9].

The limitations of TEOS, including its lower efficiency in carbonate substrates, could be overcome by phosphate-based consolidants. Though TEOS can bond with the silicate fractions in the calcareous substrates, the mineralogical differences result in incoherent gel formation [14]. An aqueous solution of inorganic diammonium hydrogen phosphate (DAP) is observed to produce better consolidation in calcareous substrates. DAP provides phosphates to react with the calcium ions from the substrates and form hydroxyapatite and other calcium phosphates, consolidating the substrate by effectively bonding the grains together. The product of consolidation with DAP – hydroxyapatite (HAP) – consolidates without significantly altering the pore size distribution and transport properties and does not make the substrate hydrophobic [12, 13]. Hence, DAP is effective in calcareous substrates with high carbonate content, whereas TEOS is effective in those with aluminosilicates and quartz to form chemical bonds. The efficiency of these consolidants in masonry systems, which are mineralogically and mechanically heterogeneous, remains less explored. Moreover, the application of consolidants onto salt-contaminated substrates is quite challenging as the presence of salt might limit the contact between the consolidant and the pore wall, reducing the bonding between them [19]. The consolidants could also dissolve the salt and migrate it within the substrate. However, the salt will not dissolve if the solvent of the consolidant is organic, and this could negatively affect the consolidant penetration as the salt blocks the pores. Also, even if the consolidant effectively penetrates the surface layer of the substrate, the cracks containing salts within the substrate will not be bridged as the consolidant will encapsulate the salt within, which could potentially worsen the damage over time [5, 20].

The consolidation efficiency is often measured through the increase in mechanical properties of the substrate post the consolidation. However, limited research relates consolidant uptake and retention of products to the pore size distribution and composition of the homogenous masonry units and heterogenous masonry systems. Hence, the primary objective of the current study is to quantify the consolidant uptake and retention of bricks, mortars, and brick-mortar sandwich specimens when consolidated with TEOS and DAP. Specimens, artificially weathered in chlorides and sulphates, were consolidated. The consolidant absorption efficiency was assessed by observing the mass increase during consolidation and comparing the ultrasonic pulse velocity before and after consolidation. Scientifically, it aims at filling the existing knowledge gap on the short-term and long-term efficiency of consolidants, focussing on the relation between the amount of consolidant ingress, amount of product retained and the associated alterations in pore size distribution for the silane-based and phosphate-based consolidants onto different masonry substrates. Practically, the findings intend to aid in informed decision-making during the selection of consolidants in masonry systems.

2 Materials and methods

2.1 Raw materials

Fired clay bricks, dry hydrated lime (DHL) powder, limestone, standard sands of zones I, II, and III as per IS 383 -2016 [21], Diammonium hydrogen phosphate (DAP), Tetraethoxysilane (TEOS), cellulose poultice and distilled water were the raw materials used in the study. The commercially procured bricks were burnt clay bricks of about 190 mm X 90 mm X 90 mm. Their compressive strength and water absorption were 7.37 MPa and 14.49 %, tested as per IS 3495:1992 [22]. The D_{50} of the dry hydrated lime powder was determined to be 11.15 µm using the Anton Paar PSA 1190 (model L) particle size analyzer. X-ray diffractograms of the raw materials revealed that DHL is rich in portlandite with traces of calcite, and the brick consists of Quartz, Alumina, Feldspar and Magnetite. Diammonium hydrogen phosphate (DAP) distributed by CTS s.r.l. and Tetraethoxysilane (BIO ESTEL New – UN 1993) by CTS s.r.l. were used as consolidants.

2.2 Specimen preparation

The cylindrical specimens of diameter 50 ± 0.5 mm and height 50 ± 0.5 mm were prepared for the accelerated salt weathering study (Figure 1). The brick specimens were made by coring from the standard brick samples. Acrylic moulds of the required size were fabricated and used to cast mortar specimens. A water-to-binder ratio of 0.85 was chosen for casting the mortar specimens, as the chosen value gave a flow of 164 mm in the flow table test as per IS 5512 – 1983 (reaffirmed in 2004) [23] and a retentivity of 89%, according to the flow retention test [24]. The mortar specimens were demoulded seven days after casting and were exposed to accelerated carbonation at 3% CO_2 (DHL-AC-28) or natural carbonation under a sheltered exposure site (DHL-NC-28). Sandwich specimens made with brick slices of 20 mm height with 10 mm thick mortar in between were exposed to accelerated carbonation at 3% CO_2 (Brick-DHL-AC-28) or natural carbonation (Brick-DHL-NC-28).

2.3 Accelerated salt weathering

The accelerated salt weathering procedure recommended by the RILEM Technical Committee – TC 271 ASC was followed [25]. Sodium chloride and sodium sulphate, at 10% and 5% by weight, respectively, were the weathering agents introduced into the substrates by capillary absorption. Specimens weathered in chloride solution are designated with a "C" suffix, and those weathered in sulphate solution are designated with an "S" suffix.

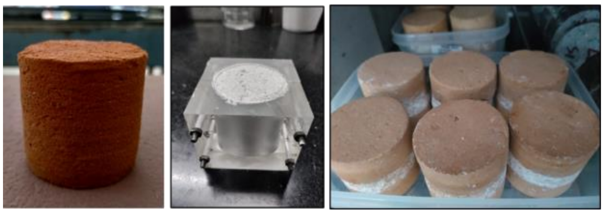

Figure 1. Specimens used for weathering and consolidation.

This study used the salt solution to re-wet the specimens instead of distilled water and introduced more salt into the system, thereby aggravating the damage. After completing two weathering cycles, the specimens were desalinated and then consolidated as per the procedure explained in section 2.4. Three months after consolidation, salt weathering of specimens was resumed in the respective environments (chloride or sulphate) to evaluate the impact of consolidation on resistance to salt weathering. However, this paper discusses the porosity data measured after salt weathering, with other findings to be addressed in future publications.

2.4 Consolidation

Salt removal through cellulose poulticing was done before the consolidation of the specimens in a similar way as would be done in the field in real cases. Powdered cellulose and deionized water at a ratio of 1:3 by weight were used to wrap the specimens completely. After drying, poulticing was removed, and the specimens were cleaned for consolidation.

For TEOS consolidation, the commercially purchased compound (viscosity ≈ 10 mPa.s) [9] was applied to the lateral surface of the desalinated specimens by brushing. Application until apparent refusal was performed, as the technical data sheet recommended. For uniformity, the number of strokes of application was limited to 50. The procedure followed for TEOS consolidation is depicted in Figure 2. The penetration of the compound to the specimen was ensured by monitoring the movement of the wet front from the lateral surface to the interior. Complete penetration of the compound was seen within 50 strokes. The TEOS-coated specimens were further cured for 28 days in the laboratory at 22 ±2°C. TEOS reaction, being a slow process, does not provide full mechanical improvement to the substrate, even after three to four weeks of curing. Also, TEOS products leave the substrate hydrophobic, preventing any further water treatment. Hence, the specimens were poulticed to remove the acquired hydrophobicity and improve their mechanical properties, thus reducing the TEOS curing time, according to the procedure proposed in [14]. The consolidation procedure ended after removing the poultice and drying the specimens in an oven at 40 °C for three days.

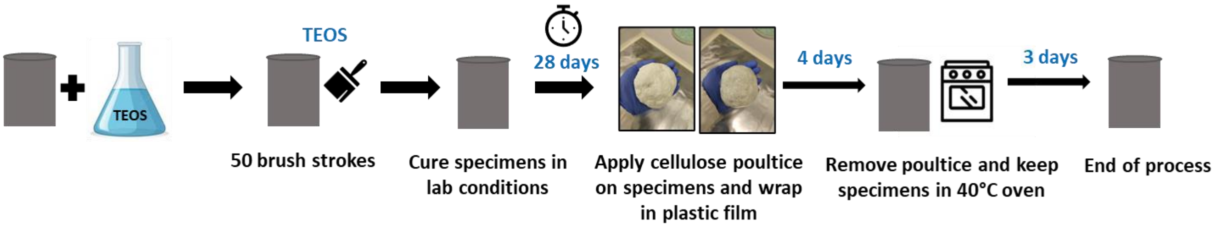

Figure 2. Procedure for TEOS consolidation.

For DAP consolidation, a 3 M DAP aqueous solution (viscosity ≈ 2 mPa.s) [9] was applied on the lateral surface of the specimens by brushing. The same number of strokes (50) as for the TEOS treatment was used, and the attainment of apparent refusal was confirmed through visual observation. The procedure followed for DAP consolidation is depicted in Figure 3. The specimens were covered with a plastic film to avoid the evaporation of the solution immediately after consolidation. The specimens were unwrapped and rinsed after 24 hours. Rinsing with water was used to remove the excess, unreacted material from the surface, thereby avoiding surface pore blockage. The specimens were then oven-dried at 40 °C for five days. Limewater poulticing was employed to provide additional Ca ions for the unreacted DAP within the specimen and to remove the excess unreacted DAP during the drying phase of poulticing [26]. $Ca(OH)_2$ concentration in water was 1.7 g/L for lime water poulticing. The mix was thoroughly stirred and further filtered to remove the traces of $CaCO_3$. Cellulose poultice:lime water solution was taken as 1:4 by weight. Cellulose poultice and the required amount of deionized water were mixed until the required workability was achieved. They were applied to the specimens after wrapping the specimens with a permeable membrane, as shown in Figure 3. The poultice-covered specimens were wrapped with a plastic film for 24 hours to avoid evaporation; then the plastic film was removed. After five days of air-drying, the poultice was removed, the specimens were rinsed to remove the surface residue of poultice and then dried.

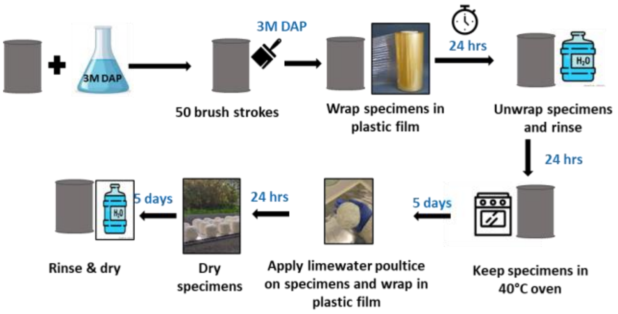

Figure 3. Procedures for DAP consolidation.

2.5 Characterization techniques

The extent of carbonation on the mortar cubes after 28 days of natural and accelerated carbonation was tested using the phenolphthalein indicator. A Servo Hydraulic Compression Testing machine was used to test the cubes for compressive strength at a loading rate of 167 N/s. The link between the strength and matrix compactness was established using the Ultrasonic Pulse Velocity (UPV) Test with transducers of frequency 54 kHz as per ASTM C597-2016 [27]. The water sorptivity test was conducted as per the South African Durability Index manual [28]. The porosity and pore size distribution of mortar specimens before and after salt weathering were studied using Mercury Intrusion Porosimetry (MIP) technique. The test was conducted using Anton Paar Quantachrome PoreMaster60 by pressuring the sample setup with mercury from 0 to about 410 MPa and analyzing using Quantachrome Poremaster software.

3 Results and discussions

3.1 Pre-weathering properties

The average compressive strength of the brick, DHL-AC-28 and DHL-NC-28 are 7.37 MPa, 0.8 MPa and 3.3 MPa, respectively. Carbonation aids strength development in lime-based mortar systems, and exposure to higher concentrations of carbon dioxide positively influences the mortar strength, as evident from the higher compressive strength of DHL-AC-28 compared to that of DHL-NC-28. Accelerated carbonation, conducted with a 3% CO_2 exposure over 28 days, resulted in complete carbonation in DHL-AC-28, confirmed by phenolphthalein indicator tests and X-ray diffraction analysis, which identified calcite as the primary phase alongside quartz from aggregates. In contrast, DHL-NC-28 retained portlandite, indicating incomplete carbonation and contributing to the lower compressive strength. The observations of the compressive strength test were complemented using an ultrasonic pulse velocity test. Accelerated carbonated lime mortar shows an average velocity of 2760 m/s, higher than 2147 m/s of the naturally carbonated lime mortar, due to the better matrix integrity of the former. The improved matrix compactness achieved through accelerated carbonation is also observed in the sorptivity values. DHL-AC-28 has a sorptivity of 66.8 mm/√hr, and that of DHL-NC-28 is 69.8 mm/√hr. The capillary porosity of 24% and 26% for DHL-AC-28 and DHL-NC-28, respectively, also indicates the reduction in porosity achieved through accelerated carbonation of mortars. According to the Mercury Intrusion Porosimetry, the porosity values of mortar samples are 27.18% and 28.23% for DHL-AC-28 and DHL-NC-28, respectively, and that of brick is 20.86%. Higher porosity revealed through MIP than water-accessible porosity is because of the high pressure allowing mercury to intrude finer pores. Figure 4 demonstrates the pore refinement attained through accelerated carbonation in lime mortar, with the cumulative intrusion curve further illustrating the reduced porosity in DHL-AC-28 compared to DHL-NC-28.

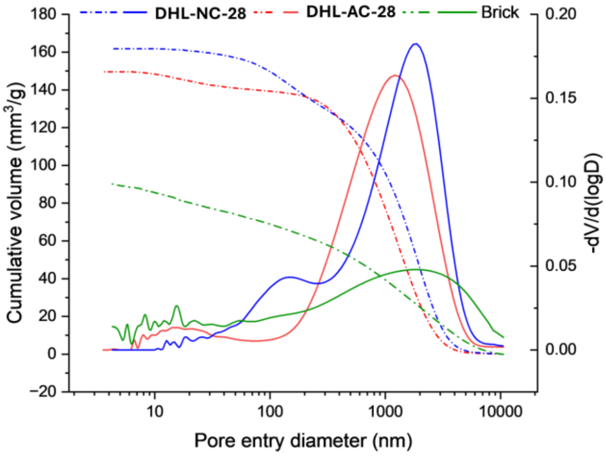

Figure 4. Differential intrusion curves (solid curves) and cumulative intrusion curves (dotted lines) of brick and mortars.
DHL-NC-28: Lime mortar, cast using dry hydrated lime powder and naturally carbonated for 28 days, DHL-AC-28: Lime mortar, cast using dry hydrated lime powder and carbonated in accelerated carbonation chamber at 3% CO_2 for 28 days.

3.2 Consolidation: Mass changes and efficiency

The mass change of each specimen was monitored after every five brush strokes, calculating the average mass per unit volume, as shown in Figure 5. Complete penetration of the consolidants into the specimens through their lateral sides was ensured through visual observation. The samples showed an increase in weight during consolidation. The change in the slope of the curves and the slope approaching zero indicates that in most of the specimens, consolidation up to apparent refusal has been achieved. Apparent refusal – the limit beyond which the substrate cannot absorb a consolidant – was observed in all specimens except DHL-AC-28-S and DHL-AC-28-C for DAP and TEOS consolidation. This could be due to the comparatively low critical pore size of the lime mortar under accelerated carbonation, which demands additional time for consolidant penetration. However, the number of brush strokes was fixed at 50 to maintain a benchmark for comparison. The results indicate that consolidation with DAP could attain apparent refusal faster, as shown by the earlier reduction in the slope of the graphs (Figure 5) compared to that during TEOS consolidation. The uptake of DAP is much faster due to its viscosity, which is similar to water [8]. Hence, comparing the product consumption, DAP was consumed more by all the specimens than TEOS within 50 brush strokes, the only exception to this observation being DHL-NC-28-S (Table 1). However, this outlier's impact is minimal when accounting for error bars (Figure 6). The consolidant uptake depends on the porosity and pore size distribution of the substrate and the consolidant properties, such as viscosity and solvent volatility [11]. TEOS, being in a volatile solvent, showed a comparatively lesser mass increase due to faster solvent evaporation.

No consistent correlation was found between the amount of product consumed by bricks and mortar of a particular carbonation and weathering condition and their corresponding brick-mortar sandwich specimen. The observations in the individual homogenous systems (i.e. brick or mortar separately) cannot be directly translated to the observations in their corresponding heterogeneous systems (i.e. brick mortar sandwich) due to the presence of the interface. Hygric resistance decelerates the moisture transport between components due to the interpenetration of the porous networks at the interface [1, 29, 30]. This additional component in heterogenous systems deviates their behaviour from the behaviour of individual components. Similarity in pore size distribution between the components is essential in reducing the interface resistance. Naturally carbonated lime mortar has a critical pore size and pore size distribution similar to brick. The pronounced difference in the pore characteristics of brick and accelerated-carbonated lime mortar could produce additional stress at the interface during salt crystallization, which forms micro fissures along the interface during the weathering procedure before consolidation. As the pores get more coarsened, more consolidants could thus be accommodated by the sandwich specimens with accelerated carbonated lime mortar than with the naturally carbonated lime mortar. Hence, sandwich specimens with accelerated-carbonated lime mortar had more consolidant uptake than their counterparts with naturally carbonated lime mortar. Additionally, it could be inferred that the pore size distribution is more crucial than the total open porosity for consolidant uptake. The significant difference in pore size distribution between the accelerated and natural carbonated systems is evident in Figure 4.

Table 1. Maximum consolidant uptake in specimens.

	Average maximum product uptake (g/cc)									
Consolidant	Brick		DHL-NC-28		DHL-AC-28		Brick-DHL-NC-28		Brick-DHL-AC-28	
	C	S	C	S	C	S	C	S	C	S
TEOS	0.23	0.22	0.11	0.25	0.21	0.24	0.20	0.22	0.24	0.24
DAP	0.29	0.26	0.17	0.21	0.31	0.30	0.27	0.24	0.28	0.27

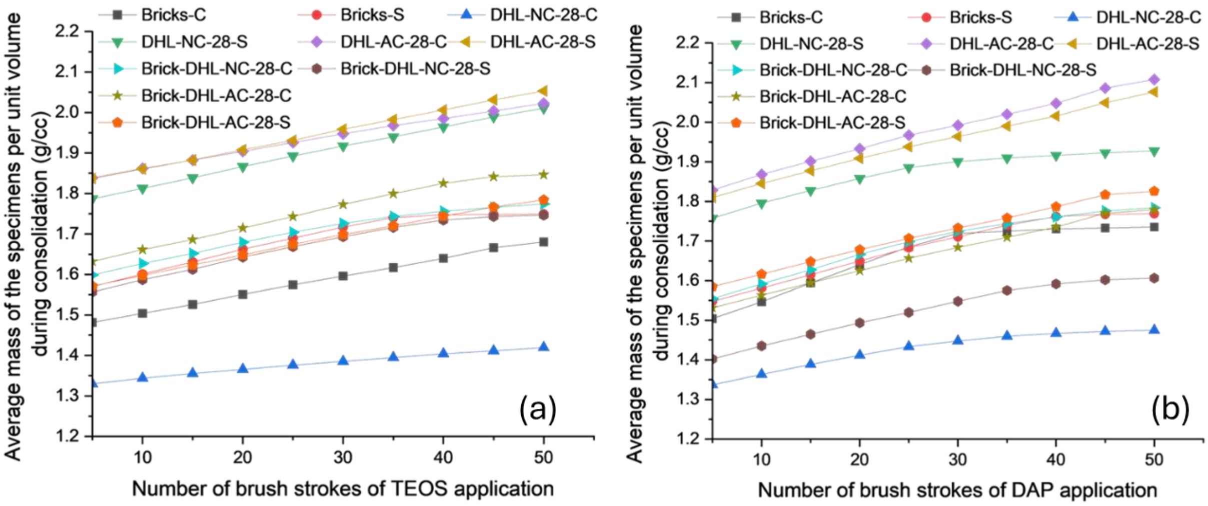

Figure 5. Average mass per unit volume of specimen during consolidation using (a) TEOS and (b) DAP.

The average maximum product uptake reflects the immediate percentage increase in the mass of the specimens (IMI) after consolidation, as shown in Figure 6. For all the specimens, except sulphate-weathered DHL-NC-28, the maximum IMI was observed for DAP consolidated specimens for both chloride-weathered and sulphate-weathered specimens. The exception, DHL-NC-28-S, however, is minor, as indicated by the error bars. Given the complete penetration of both the consolidants and the standardized number of strokes during application, the higher IMI in DAP-consolidated specimens could be attributed to two main factors – density and solvent type. DAP in its powder form has a density of 1.619 g/cc. A 3M DAP solution exhibits a density of 1.15 g/cc, which is notably higher than the density of the TEOS solution at 0.92 g/cc. Additionally, DAP uses water as its solvent, which is less volatile than the white spirit solvent used in TEOS, contributing to the observed difference.

Among the consolidated substrates of different porosities and pore size distribution, the IMI is more pronounced in brick samples, which is seemingly counterintuitive, considering the lower porosity of bricks. The pore size distribution of brick is more heterogeneous and contains larger macropores, as confirmed in Figure 4. The higher IMI in bricks compared to mortars can be attributed to the coarser pores and less tortuous pore structure, promoting faster initial uptake. This observation aligns with several research outputs stating the quicker consolidant penetration facilitated by larger pores despite their low capillary suction potential. This efficiency is due to lesser frictional resistance, high surface tension, high sorptivity and low viscosity [5, 8, 9, 12]. On the contrary, despite their high porosity and compatibility with DAP, mortars have finer pores and more tortuous networks, which hinders the immediate inflow of consolidants and reduces IMI. The IMI of brick specimens under DAP consolidation, more pronounced than that of DAP-consolidated mortars, could also be attributed to the coarser pores facilitating quicker penetration during DAP application.

Analyzing the sandwich specimens, the IMI of chloride-weathered sandwich specimens is between the IMI of brick and corresponding mortars, whereas the sulphate-weathered sandwich specimens show an increased IMI compared to their individual components. The difference in the crystallization mechanism of chlorides and sulphates could address the distinct behaviour. Chlorides occupy the pores and powder the surface on weathering with limited microcracking, whereas sulphates undergo phase transition accompanied by volumetric expansion, creating micro fissures. Considering the mechanism of sulphate crystallization, micro fissure development at the brick-mortar interface of sandwich specimens is additional to the weathering effects on their components. They create additional pathways for consolidation entry; therefore, the IMI of sulphate-weathered sandwich specimens is higher.

From the observations on product uptake and mass increase of specimens (Table 1 and Figure 6), it is evident that TEOS uptake is higher in most sulphate-weathered specimens compared to those weathered in chloride. The residual microstructural variations due to sulphate weathering, including micro-fissure development, can support this observation. However, in systems with more number of larger pores, such as brick, the development of micro-fissures may be limited, leading to similar TEOS uptake in chloride and sulphate-weathered specimens. The IMI resulting from DAP consolidation remains consistent across systems exposed to different weathering agents.

The IMI is lesser than the open porosity of the specimens, measured through pressurized mercury intrusion and capillary water absorption. This difference is due to the absence of applied pressure during consolidation and differences in the inherent viscosity of the solvent relative to water.

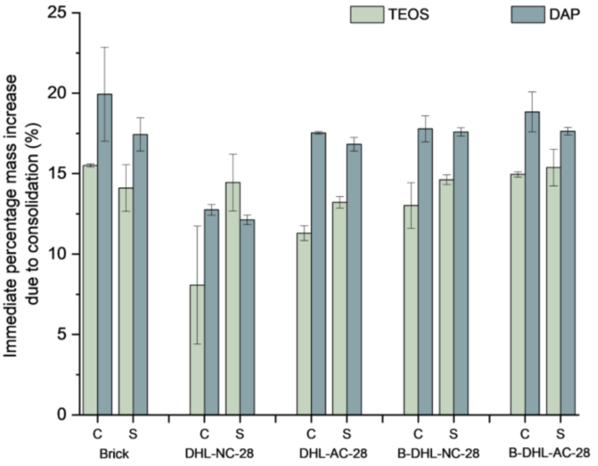

Figure 6. Immediate percentage mass increase due to consolidation.

3.3 Ultrasonic pulse velocity

The ultrasonic pulse velocity of the specimens was measured after completion of the consolidation procedure (2 weeks and 5 weeks for DAP and TEOS, respectively), and it shows a distinct pattern compared to IMI%. The formation of amorphous silica gel in TEOS-consolidated specimens and its effect on matrix densification is evidenced in the significantly higher UPV post the TEOS consolidation compared to the DAP-consolidated specimens (Figure 7). In brick specimens, TEOS consolidation resulted in a substantial increase in the UPV values, which can be attributed to both physical and chemical bond formation of TEOS with the brick substrates. Ethyl silicate establishes chemical bonds with the silicate-rich brick substrate, improving cohesion and depositing amorphous silica gel within the pores, ensuring additional chemical bonding with the substrate. Therefore, the compositional similarity between the substrate and the consolidant enables the physico-chemical action and significantly improves UPV values.

For mortar specimens, the UPV increase following TEOS consolidation was comparatively smaller. This is anticipated, as the silica source in mortars is primarily non-reactive aggregates, limiting chemical interactions. Consequently, TEOS primarily produces physical consolidation to mortar specimens by forming independent silica networks. Even though the quartzitic fractions in the lime mortar aid the formation of a chemical bond, as seen in the literature [9, 11], their limited availability makes the physical bond the dominant factor influencing UPV.

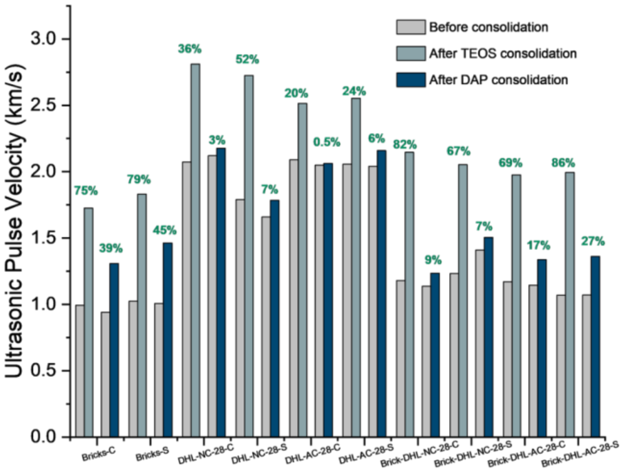

Figure 7. Ultrasonic pulse velocity of the unconsolidated and consolidated specimens.

Among the DAP consolidated specimens, DHL-NC-28 has a higher increase in UPV values than DHL-AC-28 despite the latter having high IMI%. This difference is attributed to the greater availability of Ca ions in naturally carbonated mortar, where uncarbonated portlandite remains more prevalent than in accelerated carbonated mortar. The lesser increase in velocity of DAP consolidated specimens compared to TEOS, including lime mortars, even after providing limewater poulticing, is observed across the specimens. As pore occlusion also causes an increase in UPV values, a reduced increase in UPV post-DAP consolidation could also indicate that the products of DAP consolidation do not occlude the pores and do not alter the microstructure as much as the products of TEOS consolidation. The product formation after DAP consolidation in mortar specimens could be increased using calcareous aggregates in lime mortars. They could serve as additional sources of calcium ions for effective hydroxyapatite formation. However, calcareous aggregates could further limit the chemical consolidation potential during TEOS consolidation.

Hydroxyapatite formation is expected to be more efficient in Ca-rich lime mortar than brick specimens with a limited supply of calcium ions. Limewater poultice was applied to overcome the limited formation of hydroxyapatite in silicate-rich substrates, boosting the increase in UPV post the DAP consolidation. The higher velocity increase in brick specimens than in mortar specimens after DAP consolidation could also be attributed to the higher IMI % in DAP-consolidated brick specimens. The coarse porosity of brick and its less tortuous pore structure, favouring high IMI%, also led to high UPV values for DAP-consolidated brick specimens.

3.4 Long-term consolidant retention

The long-term consolidant retention percentage, calculated 3 months after consolidation, presents a different trend than IMI%. TEOS-consolidated specimens exhibit notably higher retention than DAP-consolidated specimens, regardless of the specimen type and weathering agent (Figure 8). Despite the higher volatility of the solvent, resulting in lesser IMI% (Figure 6), the efficient formation of inert silica gel in the pores of the specimens has resulted in a higher percentage of consolidant retention for TEOS-consolidated specimens, as observed previously in the literature [8]. The observations indicate the formation of durable by-products with silica networks of high integrity due to TEOS consolidation. The aluminosilicates in the brick aid the formation of Si-O-Si bonds after TEOS application [5, 6, 14]. Precipitation of amorphous silica, which connects loose grains and occludes the pores, contributes to the mass gain.

Similar to the silicate-rich brick, the calcium-rich lime mortar also showed a higher retention percentage after TEOS consolidation. Two inferences can be drawn from this observation, one regarding the type of product on TEOS consolidation of lime mortar and the other on the amount of product formed. Due to silica-rich aggregates facilitating physical and chemical bonding between TEOS and the substrate, TEOS could primarily consolidate the lime mortar specimens. The probability of having silanol groups available on the quartz surface is limited, and the quartz crystals are often well embedded in the lime matrix. Hence, rather than the bonding capability at this molecular level, the pore-filling capability by forming an independent silica network is more predominant in the TEOS consolidation of lime mortar. However, the higher retention percentage in TEOS-consolidated lime mortar suggests that the volume or amount of silica gel formed is significantly higher, compensating for its lower molecular weight. In contrast, DAP consolidation bridges the calcium ions and does not occlude pores as effectively, resulting in lower retention.

The typical reaction between DAP and calcium ions from the substrates forming HAP can be summarized below [15]:

$$10CaCO_3 + 5(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4,CO_3)_6(OH,CO_3)_2 + 5(NH_4)_2CO_3 + 3CO_2 + 2H_2O \quad (1)$$

During the formation of HAP, the generation of by-products that evaporate from the system also reduces the retention percentage of DAP. The volatile by-products during the hardening of TEOS – ethanol and water – also reduce the long-term retention percentage of the consolidant [31]. However, the reduction in the former is significantly more than in the latter case. It could be confirmed that DAP and TEOS have notably different product retention in the long term. The retention trend is similar in different porous systems for DAP and TEOS. Despite the low IMI %, the maximum retention percentage observed in natural carbonated lime mortar under DAP and TEOS consolidation can be attributed to its higher porosity offering space for silica gel formation during TEOS consolidation and higher availability of Ca ions, than accelerated carbonated system, for HAP formation.

The retention % of sandwich specimens is independent of the retention % of individual components. It is to be noted that the retention percentage of DAP is minimal for the sandwich specimens, even lower than the brick specimens, which is intriguing and warrants further investigation. The primary inference indicates limited desalination efficiency in brick-mortar sandwich systems, affecting product formation after consolidation. Despite having a 10 mm-thick mortar layer, which could help hydroxyapatite formation, the brick-mortar interface housing salt crystals could have interfered with the effective formation of hydroxyapatite in the sandwich specimens. Contact between the specimen surface and DAP is essential for the hydroxyapatite formation, whereas pore filling through amorphous silica formation during TEOS consolidation could be achieved even in the presence of salt within the pores. Hence, the issue of lower retention percentage is not observed in TEOS consolidated sandwich specimens. The negative retention percentages observed in some sandwich specimens, as highlighted by the error bars, suggest material degradation following consolidation. This further corroborates the presence of salts within the sandwich systems during the consolidation process. In addition to the primary inference, the differential absorption of the consolidant could also be a reason for the observed. Although full penetration was ensured through visual observation of the progression of the wetting front on the top surface of the specimen, differential absorption of the individual components could have resulted in uneven distribution and limited penetration of the consolidant near the interface. The interpenetration of the pore structure of the brick and the mortar causes hygric resistance and restrains the smooth penetration of the consolidant. This could result in the preferential filling of the consolidant at the outer pores of the specimen, limiting the availability of reactive sites to form hydroxyapatite.

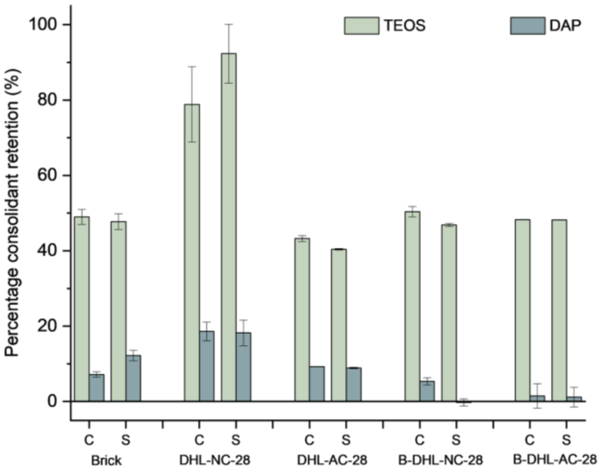

Figure 8. Percentage retention of consolidants.

The findings highlight that TEOS and DAP consolidation strategies differ in their effects on matrix structure. The observations conclude that, even though the matrix gets strengthened with consolidation using TEOS and DAP, strengthening is achieved without significant pore occlusion in DAP consolidation, whereas TEOS consolidation leads to pore refinement. This conclusion agrees with the observations from the previous works indicating significant pore structure alteration post TEOS consolidation and limited alteration post the DAP consolidation [7, 8, 12, 20, 32]. The porosity characteristics are critical to the durability of the material and the structure, as they govern the transport parameters, breathability of the system, stress generated during freeze-thaw cycles and salt crystallization [5]. Research shows that stress generation in the small pores is considerably higher and detrimental to the system than in larger pores, especially during salt crystal nucleation and growth. Larger pores enable unrestrained crystal growth, whereas smaller ones restrain crystal growth towards some directions, imparting stress that can deteriorate the pore walls [1, 33–35].

Consolidation generally increases microporosity and reduces the number of larger pores. As the number of pores of radius less than 1 µm increases, the susceptibility due to damage during salt attack also increases [7, 16]. The pore structure alteration by TEOS consolidation on mortars was captured after consolidation and subsequent salt weathering using Mercury Intrusion Porosimetry (Figure 9). The critical pore size shifts leftward, indicating pore refinement, and the volume of pores of diameter less than 0.1 µm increases post the TEOS consolidation of DHL-NC-28 mortar specimens. The distribution also shifts from unimodal to bimodal, indicating the presence of two critical pore sizes after TEOS consolidation, 40 nm and 1000 nm in DHL-NC-28-C and 20 nm and 1000 nm in DHL-NC-28-S. Such alterations are not seen in the specimens post the DAP consolidation, and the pore size distribution post the weathering of DAP consolidated specimens is similar to that of unconsolidated specimens. However, the observation regarding pore structure alteration on TEOS consolidation is limited to naturally carbonated mortar and not found in the accelerated carbonated system, indicating the need for further investigation. As indicated by the cumulative pore volume, porosity presents an interesting trend. The porosity of the consolidated specimens subsequently weathered in sulphate solution after consolidation is lower than that of unconsolidated specimens. Consolidants improve the overall cohesion and strength of the substrates and do not develop micro-fissures due to the stress generated through volumetric expansion during sulphate weathering as easily as unconsolidated specimens. Thus, the porosities of consolidated specimens are lower than the sulphate-weathered control specimens. However, the graphs indicate possible detrimental effects of reduced critical pore size during salt weathering and freeze-thaw.

4 Conclusions

This study systematically evaluated the consolidation efficiency of DAP and TEOS on various masonry components, assessing parameters such as product uptake, immediate mass increase (IMI%), retention percentage, ultrasonic pulse velocity and impact on porosity. The observations on individual components and masonry sandwiches revealed notable distinctions in the consolidation behaviour of homogenous and heterogenous systems.

i. The lower viscosity and lower volatility of the solvent ensure easy penetration of the DAP solution, and the substrates attain faster apparent refusal than those of the TEOS application.

ii. The higher density of the DAP solution and the presence of volatile solvent in TEOS results in a higher immediate increase in the mass of specimens during

DAP consolidation than TEOS consolidation. Pore size distribution of substrate is important, along with its porosity, in ensuring product uptake. Heterogenous pore structures with larger pores facilitate the efficient transport of consolidants, as observed in brick and brick-mortar systems.

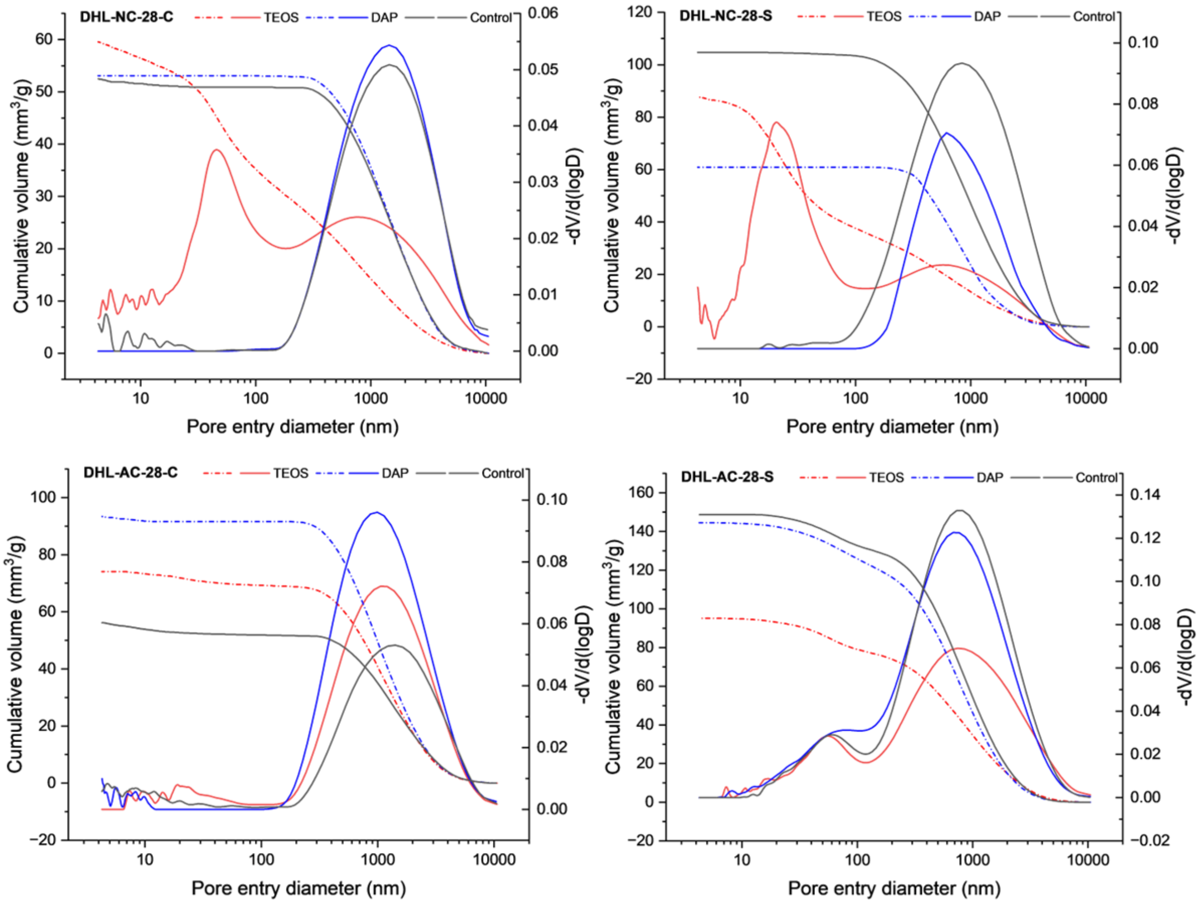

Figure 9. Cumulative intrusion curve and differential intrusion curve of specimens post consolidation and weathering.

iii. DAP consolidates the substrates without significant pore occlusion, therefore preserving the microstructural integrity. In contrast, TEOS consolidation results in the formation of silica gel, which significantly alters the microstructure. The observations indicate that while TEOS consolidation demonstrates high efficiency, it often leads to pore occlusion, which could negatively impact the durability of materials exposed to salt weathering and freeze-thaw cycles.

iv. The extensive improvement in the matrix integrity offered by TEOS consolidation is not limited to silicate-rich substrates. In the absence of reactive silicates, forming physical bonds with substrates forming independent silica networks ensures effective consolidation. Hence, the consolidant retention percentage of TEOS was significantly higher than that of DAP.

v. DAP demonstrates limited retention in heterogeneous systems like brick-mortar sandwiches, likely due to interfacial hygric resistance that reduces consolidant distribution across the substrate.

vi. The observations on the consolidation efficiency of individual systems do not directly translate to that of the heterogeneous systems made with the individual components. This observation emphasizes the need for tailored approaches when consolidating heterogeneous substrates.

The results underscore the critical role of pore size distribution and porosity in the initial product uptake and the significance of compositional similarity between the substrate and the consolidant in the long-term retention of the consolidants. While providing more substantial initial matrix integrity through pore refinement, TEOS may face potential long-term durability challenges, especially in freeze-thaw or salt-exposed environments. Conversely, DAP offers consolidation with minimal structural alteration, preserving pore structure and ensuring material breathability—traits valuable for applications requiring the preservation of original material properties. These findings provide a foundation for selecting appropriate consolidants for masonry systems, especially in conservation applications sensitive to both structural and environmental stressors.

Acknowledgements

The authors would like to gratefully acknowledge the funding from the Ministry of Education, Government of India, towards the Fellowship of the first author. The authors are grateful to the Building Technology and Construction Management (BTCM) Division, Department of Civil Engineering at Indian Institute of Technology Madras, India, and DICAM laboratory at the University of Bologna, for providing the laboratory facilities.

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