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Segment on

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Edited by
Inge Rörig-Dalgaard and Ioannis Ioannou

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Historical Masonry
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RILEM was founded in 1947, and has a membership of over 900 in some 70 countries. It forms an institutional framework for co-operation by experts to:

- optimise and harmonise test methods for measuring properties and performance of building and civil engineering materials and structures under laboratory and service environments,
- prepare technical recommendations for testing methods,
- prepare state-of-the-art reports to identify further research needs,
- collaborate with national or international associations in realising these objectives.

RILEM members include the leading building research and testing laboratories around the world, industrial research, manufacturing and contracting interests, as well as a significant number of individual members from industry and universities. RILEM’s focus is on construction materials and their use in building and civil engineering structures, covering all phases of the building process from manufacture to use and recycling of materials.

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PRO 108: Innovation of Teaching in Materials and Structures

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PRO 110: Historical Masonry

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PRO 112: Moisture in Materials and Structures

PRO 113: Concrete with Supplementary Cementitious materials

PRO 114: Frost Action in Concrete

PRO 155: Fresh Concrete

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Preface

The conference “Materials, Systems and Structures in Civil Engineering – MSSCE 2016” is part of the RILEM week 2016, which consists of a series of parallel and consecutive conference and doctoral course segments on different topics as well as technical and administrative meetings in several scientific organizations. The event is hosted by the Department of Civil Engineering at the Technical University of Denmark and the Danish Technological Institute and it is held at the Lyngby campus of the Technical University of Denmark 15-29 August 2016.

This volume contains the proceedings of the MSSCE 2016 conference segment on “Historical Masonry”. This conference segment has been organised to revitalise interest in Historical Masonry within the RILEM community. Historical structures comprise a major part of our architectural and cultural heritage. Despite the fact that one may get the impression that these structures have been there forever and therefore have a never-ending history, the truth is somehow different. Historical structures need extra care and continuing attention to survive in the changing and challenging environment they are exposed to. At the same time, the complexity of these structures, in the form of construction materials and typologies, adds to the difficulty in approaching them effectively and efficiently. Special demands are therefore imposed upon academics and practitioners who work with historical masonry structures in order to maintain their durability, without affecting their original character.

In view of the above, the present conference segment deals with theory, modelling and results from experimental investigations within the wider field of Historical Masonry. The topics covered include masonry materials (characterization and reproduction), measurement techniques, mechanisms of masonry decay and methods of assessing and protecting masonry. Papers featuring in the proceedings present state-of-the-art knowledge that extends to some interesting case studies. All contributions have been peer-reviewed thanks to the voluntary work of the members of the scientific committee and a select group of colleagues around the world.

Despite the fact that we had to compete against a number of other major conferences in the field, also taking place in 2016 (e.g. Terra, IBMAC, Stone Congress and HMC), we managed to get together a significant number of participants from all over Europe and USA, thus making the Historical Masonry conference segment one of the busiest events during the RILEM Week. We would therefore like to thank each and every one of the contributors for their input and attendance and for inspiring discussions on the topic we are all very much interested in. Special thanks to our 2 distinguished keynote speakers (Profs G.W. Scherer and P.B. Lourenco). Their presence in Lyngby will surely contribute to make this conference a success.

Working together to create a platform for collaboration on Historical Masonry has been a joy! We hope that you will also enjoy the conference and your stay in Denmark. May this conference segment be the starting point for increased activity within RILEM in the field of Historical Masonry!

Yours sincerely
Inge Rörig-Dalgaard & Ioannis Ioannou

XI
Welcome

Were you aware that a part of your daily language is likely to be in Danish? A thousand years ago the Danish word “Vindue” came along with the Vikings to England. Several hundred years later it reached North America, and from there – just two to three decades ago – almost every person in the world learned to understand and pronounce this word: “Windows”, which etymologically means “an eye to the wind”.

As a child your career as construction professional may have started with LEGO, and before you went to bed, your mother told you the unforgettable fairytales of H.C.Andersen. You may have grown up with the delicious taste of Lurpak butter on your bread, and though you might find it strange that “God plays dice with the Universe”, hopefully your school teacher told you that on this topic Einstein was flat out wrong and Niels Bohr was right. Right now you may prefer to be sitting in the sun with a chilled Carlsberg beer in your hand, enjoying the iconic view of the Sydney Opera House. All of it is Danish made, and many things around you at home, if not made in Denmark, were probably brought to you by Maersk, the world’s largest shipping company, the modern Danish Viking fleet.

Though Denmark is one of the world’s smallest countries, yet it stands – along with your country – among the greatest. On top of a thousand years of outreach from Denmark, your visit to the Danes is most welcome. On your approach to Copenhagen airport you had a view to wind turbines harvesting green energy, you saw record breaking bridges, and perhaps you got a glimpse of the island Ven where the nobleman Tycho Brahe literally speaking changed our view of the world through perfection of astronomical observations with his naked eye. In Copenhagen you may appreciate a walk in the fairytale amusement park TIVOLI, and in the Copenhagen harbour you may have a rendezvous with a Little Mermaid.

Of all things in Denmark you will surely enjoy the conference and doctoral courses Materials, Systems and Structures in Civil Engineering, MSSCE 2016 which are held in conjunction with the 70th annual RILEM week. On this occasion RILEM celebrates its 70 years birthday and thus maintains generations of experience. However, new activities and the in-built diversity keep RILEM fresh and dynamic like a teenager.

The event takes place in northern Copenhagen, Lyngby, at the campus of the Technical University of Denmark, 15-29 August 2016. MSSCE 2016 aims at extending the borders of the RILEM week by including doctoral courses, by involving a palette of RILEM topics in the conference and workshop activities, and by collaborating with other scientific organizations. The insight and outlook provided by this event make it RILEM’s technical and educational activity window.

It is a pleasure to share with you what is unique to RILEM and Denmark!

Ole Mejlhede Jensen, Technical University of Denmark
Honorary president of RILEM 2016, Chairman of MSSCE 2016
MINERAL CONSOLIDANTS

George W. Scherer (1), Enrico Sassoni (2)

(1) Princeton University, Princeton (NJ), USA
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Abstract
Inorganic consolidants, such as ethyl silicate, nanolime and ammonium oxalate, have proven to be effective for certain materials, but each has its drawbacks. This has recently led to the investigation of hydroxyapatite (HAP) as a novel inorganic consolidant, which demonstrated excellent performance on carbonate stones. Considering that a mineral that matched calcite crystal lattice parameters even more closely than HAP would be expected to provide a consolidating action even greater than HAP, in this study aluminum phosphate (AP) was investigated as a potential new consolidant. Indeed, AP has lattice parameters differing from those of calcite by only 1%. The consolidating ability of AP was preliminarily investigated here in comparison with HAP. Both treatments were tested on artificially weathered marble samples, in the view of their application for conservation of sugaring marble. A novel method is also proposed for producing samples with near-surface damage similar to that of sugaring marble in the field. The results of the study point out that the novel weathering method is able to provide samples with tailored gradient in dynamic elastic modulus, closely resembling naturally sugaring marble. The AP treatment was found to significantly improve the dynamic elastic modulus of weathered marble, at least as efficiently as the HAP treatment investigated in this study. This confirmed the high potential of AP as a new inorganic consolidant.

1. Introduction
Consolidation is often needed to restore mechanical properties of stones used in historic masonry and decorative architectural elements, which undergo deterioration because of chemical-physical processes (such as freezing-thawing cycles, salt crystallization, swelling of clays). Organic consolidants, such as acrylic and epoxy resins, were widely used in the past, because of their good adhesive properties and strengthening ability. However, their behavior over time has proven to be substantially unsatisfactory, because of their tendency to change
color, their sensitivity to UV light and their generally low durability [1]. Consequently, research has recently mainly focused on inorganic consolidants. Silicate consolidants, such as TEOS-based products, have a good ability to strengthen silicate substrates (sandstones, but also fired clay bricks) [2-4]. Thanks to the chemical bonding between the silica gel formed by TEOS hydrolysis and condensation and the hydroxyl groups present on the surface of silicate substrates, a remarkable increase in mechanical properties can be achieved after consolidation. However, the efficacy of TEOS-based consolidants is significantly lower in the case of carbonate stones, such as porous limestone and marble (widely used for masonry blocks and decorative elements, respectively). As carbonate stones lack hydroxyl groups on their surface, only physical-mechanical interlocking can take place between the consolidant and the substrate, which results in limited consolidating efficacy [2,3]. A further limitation of silicate consolidants, independent of the substrate, is that TEOS hydrolysis-condensation reactions take a long time to be completed (even more than 6 months) [3]. As a consequence, the treated stone remains hydrophobic for a long time, which can be undesirable in case water-based treatments need to be applied after consolidation or in case water is trapped behind the hydrophobic layer. To accelerate TEOS hydrolysis-condensation reactions, innovative methods have recently been proposed, based on stone treatment with water or water-ethanol mixtures to favor substitution of ethoxy groups with hydroxyl groups [5,6].

In the case of carbonate stones, a potentially highly compatible consolidant is lime, which turns into calcium carbonate upon carbonation. To overcome the limitations of traditional lime-based treatments, such as impregnation with limewater and lime-milk (viz., low solubility of lime in water, need of repeated applications, slow carbonation process, low penetration depth), nanolimes have recently been proposed [7]. Thanks to their nanometric size, the carbonation process is faster and the penetration depth is expected to be higher. Nonetheless, since lime nanoparticles tend to agglomerate, particles accumulate near the surface and consequent whitening of the treated stone is frequent. To improve these aspects, several strategies are currently under investigation, such as tuning of the solvent used for particle dispersion [8].

An alternative treatment for consolidation of carbonate stones is that based on calcium oxalate formation. By treating stone with an aqueous solution of ammonium oxalate, calcium oxalate is formed by reaction with the calcitic substrate. The treatment, originally proposed for wall painting conservation [9], has been found to provide a good protective action to marble surfaces [10]. The formation of a coherent and non-porous layer of calcium oxalate over calcite is indeed able to increase stone resistance to dissolution in rain; however, the solubility of calcium oxalate is similar to that of calcite, so its long-term benefits are not yet clear. The treatment has proven to offer only a minor improvement in mechanical properties of treated marble, likely because of the limited depth of calcium oxalate formation [11].

Taking inspiration from the calcium oxalate treatment, in 2011 we proposed a novel consolidant for carbonate stones, based on formation of hydroxyapatite (HAP, Ca$_{10}$(PO$_4$)$_6$(OH$_2$)) [12]. HAP is formed by treating the calcitic substrate with an aqueous solution of diammonium hydrogen phosphate (DAP). With respect to the calcium oxalate, HAP has the advantage of having a much closer match with calcite in terms of lattice
parameters and a much lower solubility and dissolution rate [12,13] (Table 1). The match between lattice parameters is important because, if a layer of HAP can be grown epitaxially over calcite, a very efficient bonding can be expected, resulting in very efficient consolidating and protecting abilities. Very encouraging results have been obtained so far on the use of HAP for consolidation of marble and limestone [11,12,15,16] and on marble protection from dissolution in rain [10,17]. However, while the 5% lattice mismatch might be small enough to favor nucleation of HAP on calcite, it is large enough to result in considerable stress if the layer grows more than a few nm thick. That may explain why the HAP deposits are not dense layers, but instead are flowery and porous [18].

To overcome the limitation deriving from the 5% mismatch between HAP and calcite lattice parameters, a different mineral would be needed, exhibiting an even closer match with calcite. As reported in Table 1, aluminum phosphate (AP, AlPO₄, the mineral berlinite) has lattice parameters differing by only 1% from those of calcite. Based on data from the literature [19,20,21], we estimate the solubility product of AP to be about 5.7 x 10⁻²², which is much lower than that of calcite (3 x 10⁻⁹). Therefore, AP has the potential of forming a strongly bonded and insoluble layer over calcite grains, thus providing protection against dissolution as well as mechanical strengthening. In this paper, we present some preliminary results on the consolidating ability of AP, in comparison with HAP. Both treatments were tested on marble samples artificially weathered to simulate sugaring marble.

Sugaring is a deterioration phenomenon that frequently affects marble, both in ancient and modern buildings [11,22]. As calcite deforms anisotropically upon heating, repeated day/night temperature excursions cause stress and micro-cracking at the boundaries between calcite grains, resulting in grain detachment and loss [23]. Sugaring mainly affects the outer surface, which is directly exposed to solar radiation and to air temperature variations, while the underlying substrate is usually undamaged. Since testing of marble consolidants requires the use of samples with physical-mechanical properties as similar as possible to those of deteriorated marble in the field [11], we have developed a new method for reproducing the near-surface damage found in sugaring marble, starting from freshly quarried marble.

Therefore, in the present paper the new method for producing artificially weathered marble samples is presented first and then some preliminary results are reported and discussed on the use of HAP and AP to consolidate weathered marble.

Table 1: Lattice parameters and solubility products of calcite, ammonium oxalate, hydroxyapatite (HAP) and aluminum phosphate (AP). Data are taken from [13] for calcite, ammonium oxalate and HAP. Lattice parameters of AP are taken from [14].

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$K_{sp}$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (2×)</td>
<td>9.98</td>
<td>9.98</td>
<td>33.82</td>
<td>$3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Calcium oxalate (2×)</td>
<td>12.58</td>
<td>29.16</td>
<td>20.32</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>HAP</td>
<td>9.43</td>
<td>9.43</td>
<td>6.88</td>
<td>$3 \times 10^{-59}$</td>
</tr>
<tr>
<td>AP (2×)</td>
<td>9.88</td>
<td>9.88</td>
<td>21.89</td>
<td>$6 \times 10^{-22}$</td>
</tr>
</tbody>
</table>
2. Materials and methods

2.1 Marble accelerated weathering

Carrara marble (provided by BasketweaveMosaics.com, USA) was used for the tests. Cubes with 5 cm edge length were wet sawn from a freshly quarried slab. To simulate the near-surface damage of sugaring marble, the core idea is to induce a gradient in marble mechanical properties by putting samples in contact with a hot plate for a certain time. In this way, the part of the sample in contact with the hot plate undergoes micro-cracking at the boundaries between grains, whereas at a certain distance from the plate marble remains unheated and hence undamaged.

To define what should be the depth to which marble should be weathered, real samples of sugaring marble from the field were considered. In real samples, sugaring was found to affect marble to a depth of about 1 cm from the surface. In this 1 cm-deep surface layer, marble ultrasonic pulse velocity (UPV, often used to characterize the conservation state of marble) was found to be reduced by about 20% with respect to the undamaged substrate [11]. Consequently, we adopted a decrease in UPV of 20% in the first centimeter from the surface as the target of our artificial weathering procedure.

To define what temperature and what heating duration should be used to produce the desired weathering level, we first correlated the heating temperature with the UPV, by heating samples at 100, 200, 300 and 400 °C for 1 hour and measuring the corresponding decrease in UPV. Having determined that the desired UPV decrease is reached by heating at 100 °C (as detailed in a future publication), the time of heating necessary to induce the UPV decrease in the first centimeter from the surface, but not in the underlying part, was calculated as follows.

Holes with increasing length were drilled in a marble cube as illustrated in Figure 1. Thermocouples were inserted into the holes to allow temperature measurement at increasing distance from the heating plate (nominally, 0, 10, 20, 30, 40 and 50 mm). The cube was put over the heating plate, initially cold, and the sides and the top were insulated using a high temperature-resistant insulator, to ensure that the heat flux was one-dimensional. The heating plate was then turned on and the temperature progressively increased up to 400 °C. Temperature variations at different distances from the plate were then measured as a function of time. In the described conditions, the equation governing the heat flow is:

\[ \frac{\partial T}{\partial t} = \frac{1}{\partial x} \left( k(x,t) \frac{\partial T}{\partial x} \right) \]  

(1)

where \( T \) is the temperature, \( t \) is the time, \( x \) is the distance from the heating plate and \( k \) is marble thermal diffusivity. We assumed the same exponential decrease of \( k \) observed in Holston marble by Hanley et al. [24]. By fitting temperature values measured at different distances from the plate to a numerical solution of Eq. (1), it was possible to calculate \( k \), which was found to vary from \(-1 \times 10^{-4} \text{m}^2/\text{s}\) at room temperature to \(-5 \times 10^{-7} \text{m}^2/\text{s}\) at 300 °C. For this variation of \( k \) with temperature, it was calculated that putting the sample in contact with the heating plate at 200 °C for 20 seconds would cause an average decrease in dynamic
elastic modulus ($E_d$, related to UPV through the density) in the first centimeter from the surface very similar to that exhibited by naturally weathered marble. The details of the model used to calculate the heating temperature and time will be presented in a future publication. The model can be used to simulate arbitrary heating procedures.

![Diagram of sample instrumentation](image)

**Figure 1.** Scheme illustrating sample instrumentation. During the heating experiment, the marble sample was surrounded by a high temperature-resistant thermal insulator.

To verify the model predictions, a 5 cm edge cube, instrumented as illustrated in Figure 1 and surrounded by a high temperature-resistant insulator, was placed over an heating plate originally at 200 °C for 20 seconds. After cooling, the UPV was measured at the two extremities of the sample (i.e. in the parts distant 0-1 cm and 4-5 cm from the heated surface). The UPV was measured by the transmission method, using a PUNDIT commercial instrument with 54 kHz transducers and a rubber couplant between the sample and the transducers. From UPV, $E_d$ was calculated as $E_d = \rho \times \text{UPV}^2$, where $\rho$ is sample density. $E_d$ values measured before and after heating were then compared.

### 2.2 Marble treatment

For the HAP treatment, an aqueous solution containing 0.1 M DAP, 0.1 mM CaCl$_2$·10H$_2$O and 10 vol% ethanol, was used. Ethanol was added in view of its beneficial effect in promoting HAP formation, as recently reported in [17]. For the AP treatment, samples were treated with a 0.1 M DAP and 0.1 mM Al(NO$_3$)$_3$·9H$_2$O aqueous solution, also containing 10 vol% ethanol. Ethanol was added because preliminary tests revealed that it resulted in a reduction in cracking of the film formed after treatment. Both the HAP and AP treatments were performed by submerging marble samples (5×5×1 cm$^3$) in 200 mL of the consolidating solutions for 24 hours. The samples were then rinsed with deionized water and dried at room temperature.

The morphology and the elemental composition of the new phases formed after treatment were analyzed by scanning electron microscope (FEG-SEM XL30 Philips), equipped with an
energy dispersive x-ray spectroscopy device (Oxford Instruments EDS probe). SEM-EDS analysis was carried out on previously undamaged marble samples.

The consolidating efficacy was evaluated on thermally weathered samples. Because the weathering method described in § 2.1 was still under development when the consolidating efficacy of AP was investigated, tests on HAP and AP were carried out on samples pre-weathered following a different method that we previously developed [12,25]. Samples were heated in an oven for 1 hour, some of the samples at 100 °C and some at 400 °C. In this way, it was possible to obtain uniformly damaged samples, having different levels of micro-cracking (more diffused micro-cracking in samples heated at 400 °C). To favor the penetration of the consolidating solutions into samples pre-heated at 100 °C, these samples were vacuum impregnated. The consolidating ability of the two treatments was evaluated by comparing UPV and $E_d$ before and after consolidation, determined as described in § 2.1.

3. Results and Discussion

3.1 Marble accelerated weathering

To verify what the mathematical model predicted (i.e. an average 20% decrease in UPV in the first centimeter of the sample put in contact with the heating plate at 200 °C for 20 seconds), these conditions were reproduced experimentally and the UPV variation measured in different parts of the sample. Although the heating plate was originally at 200 °C, upon contact with the sample the temperature rapidly decreased, so that after 20 seconds of contact the surface temperature reached 140 °C. For heating at 140 °C, the $E_d$ reduction is expected to be about -50% (based on the correlation between temperature and $E_d$ variation, that will be presented in a future publication). As the surface was heated at 140 °C and, at a distance of 1 cm from the surface, the temperature was still basically unchanged (maximum temperature 39 °C), the average variation in $E_d$ in the first centimeter from the plate was expected to be about -25%.

The UPV measurements after the heating experiment provided a good confirmation of the expected results. Indeed, while the part of the sample between 4 and 5 cm from the heated surface exhibited no $E_d$ variation, the first centimeter in contact with the plate exhibited an $E_d$ decrease of -29%, in good agreement with what was expected. A more continuous profiling of the damage induced by heating on the plate can be provided by nanoindentation tests, carried out at increasing distance from the heated surface. These tests are currently in progress.

3.2 Marble treatment

The morphology and the elemental composition of the new phases formed after treatment are illustrated in Figure 2, where untreated marble is also reported for comparison's sake. After the HAP treatment, the marble surface uniformly exhibits a new flowery morphology, typically ascribed to HAP. Accordingly, the EDS spectrum reveals the presence of P, alongside Ca and O. The coating appears as continuous, without uncovered areas, and uncracked. This can be ascribed to the beneficial effect of ethanol on HAP crystallization [17]. In fact, for the same DAP and CaCl$_2$·10H$_2$O concentrations, but without ethanol addition, uncoated areas remain and microcracks are present in the film.
In the case of the AP treatment, no apparent alteration of the original marble morphology is visible (Figure 2c). Nonetheless, EDS spectra acquired in different positions reveal well defined peaks of Al and P. As these peaks are clearly visible even after sample rinsing with water at the end of the 24 hour treatment, the formation of a new phase is suggested (if Al and P were owing to some compound simply deposited over marble surface, they would be washed away by rinsing). Notably, the Al/P weight ratio acquired in different positions ranges from 0.43 to 0.54, hence it is close to the 0.87 Al/P weight ratio of stoichiometric AlPO₄. This is important, considering that in the consolidating solution the DAP concentration was 1000 times higher than that of Al(NO₃)₃·9H₂O (0.1 M and 0.1 mM, respectively). This further suggests that a new phase, with a composition fairly close to that of AlPO₄, was formed after the treatment.
In terms of consolidating ability, the $E_d$ variations after heating and after consolidation are illustrated in Figure 3. As expected, heating at 400 °C caused significant additional damage compared to heating at 100 °C (average $E_d$ decreases of -94% and -32%, respectively).

In the case of HAP, $E_d$ increases of +18% and +143% were found after consolidation for samples pre-heated at 100 and 400 °C, respectively (Figure 3). This trend in consolidating ability (higher percentage increase in $E_d$ for more decayed samples) is consistent with previously obtained results on limestone consolidation by HAP [12]. Although the $E_d$ increases were remarkable, still the initial $E_d$ was not fully restored after consolidation. In previous studies on consolidation of sugaring marble by HAP, full recovery of the original $E_d$ was achieved [11,26]. The different results obtained in the present study are thought to derive from the different formulation tested here: whereas in the cited studies full $E_d$ recovery was obtained by using a higher DAP concentration [11] or a double DAP solution applications [26], in the present study a single application of a diluted DAP solution was performed.

In the case of the AP treatment, $E_d$ increases of +24% and +280% were found for samples pre-heated at 100 °C and 400 °C, respectively (Figure 3). Similarly to the case of HAP, the AP treatment exhibited the highest strengthening ability on the highly damaged substrate, even if full recovery of the initial $E_d$ was not achieved. Based on these results, the AP treatment exhibits a consolidating ability superior to that of the HAP treatment, at least in the case of the HAP formulation tested in this study. The AP treatment is hence confirmed as highly promising and future optimization (in terms of aluminum and phosphate precursors, addition of chelating agents to increase the precursors concentration, pH control, etc.) is expected to significantly improve its consolidating ability.

4. Conclusions

In this study, we presented a novel method for producing artificially decayed samples with properties resembling those of naturally sugaring marble and we reported the first results on the use of aluminum phosphate for consolidation of weathered marble.
The new artificial weathering method is based on production of near-surface damage in marble samples by contact with a hot plate at a certain temperature and for a certain time, which can be calculated by a mathematical model. The method proved to be capable of providing samples with a gradient in ultrasonic pulse velocity and dynamic elastic modulus that closely matches that of naturally weathered marble. In the future, the mathematical model can be used for simulating arbitrary heating procedures.

The aluminum phosphate treatment was found to cause a significant increase in the dynamic elastic modulus of weathered marble, the consolidating efficacy varying as a function of the initial level of damage in marble. The aluminum phosphate treatment was found to be more effective than the hydroxyapatite treatment, tested here in a new formulation for the first time. The potential of the new aluminum phosphate treatment is hence confirmed as very high and a further improvement of its consolidating ability is expected in the future from treatment optimization (in terms of aluminum and phosphate precursors, addition of chelating agents to increase the precursors concentration, pH control, etc.).

Acknowledgments
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BEHAVIOR OF HISTORIC MASONRY STRUCTURES SUBJECTED TO BLAST: TESTING, CONSTITUTIVE MODELING AND APPLICATIONS

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Abstract

In general, terrorism is defined as a pre-planned, deliberate and criminal act of violence against targets including civilians, infrastructures, public services, and information, to create terror and influence the people. Depending upon the detonating charge weight, blast site situation and site crowd, the terrorist attacks can bring a wide range of casualties and material losses.

The strain rate effect influences the properties of most construction materials. However, studies on masonry materials such as clay bricks cannot be found in the literature easily. Understanding the strain rate effect on masonry materials is important for proper modelling and assessment of masonry structures under high velocity impacts or blast loads. A Drop Weight Impact Machine will be used to obtain the strain rate effect on the ultimate strength, Young’s modulus and strain at ultimate strength. Subsequently, a newly developed test setup for dynamic out-of-plane loading using under Water Blast Wave Generators as loading source will be presented. This allows a wide range for the produced blast impulse and surface area distribution. It also avoids the generation of high velocity fragments and reduces atmospheric sound wave.

In addition, a dynamic constitutive material interface model and an anisotropic model with high strain rate effects, implemented in the finite element code ABAQUS as a user subroutine, will be presented. First, the models’ capabilities are validated with numerical simulations of unreinforced block work masonry walls subjected to impact, with relevant conclusions. Finally, applications are shown to the railway infrastructure in Portugal and the Al-Askari shrine in Iraq, which was subjected to two attacks.
NUMERICAL STUDY ON THE SEISMIC PERFORMANCE OF ADOBE VAULTED ARCHITECTURE: A CASE STUDY FROM IRAN

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(2) Escola Superior Gallaecia, Vila Nova de Cerveira, Portugal
(3) University of Colima, Colima, Mexico

Abstract
Past earthquakes prove that adobe vaults, as traditional roofing systems for adobe architecture located in hot and dry areas, play a significant role in the seismic behaviour of adobe buildings. This paper reports the results from a geometrical survey carried out on 60 traditional adobe vaulted houses from the city of Yazd, Iran, followed by a simplified seismic assessment. To this end, a reference vault combination is considered as representative of the sample. Limit analysis theory implemented in Block2D software, is employed to carry out the numerical analyses. Results indicate that parameters such as vault span, vault rise, supporting wall thickness and mechanical properties of adobe masonry have significant influence on the safety factor.

1. Introduction

Iran, with a vast number of historical adobe constructions, is located on the Alpine-Himalayan earthquake belt, one of the most seismically active areas of the world. Historically, the city of Yazd, with a large number of adobe monuments and vernacular architecture, possesses a great built heritage legated by ancient cultures and civilizations from various historical periods. Yazd has a vast number of traditional adobe houses with adobe vaults, where most of them still exhibit a good condition and are in everyday use. The relatively high seismic hazard of Yazd, with a peak ground acceleration of 0.25g, in addition to the seismic vulnerability of the adobe vaulted houses, gives rise to an urgent need for evaluating their behaviour under seismic actions.

Based on literature, most of the seismic studies on adobe constructions have focused on adobe case studies [1-3], mechanical behaviour of adobe units and prism [4-6], adobe walls [7, 8] and scaled adobe structures with wooden pitched or flat roofs [9-12]. In spite of adobe vaults vulnerability during past earthquakes, only a limited number of studies on seismic behaviour
Aiming at assessing the seismic safety of adobe vaulted houses located in Yazd, 60 houses were initially chosen as representative of existing adobe houses. A typological and geometric characterization of the vaulted constructions under study was performed in order to define the reference vaults combinations as representative of the samples. Afterwards, a numerical parametric study was conducted adopting the limit analysis theory implemented in Block2D software [17].

2. Geometrical study

The majority of adobe vaulted houses of Yazd dates back to the Qajar period (1785–1925). One of the most important features of adobe historical houses in Yazd is related to their shape, which is inward looking centralized by a courtyard and all the openings are organized around it. The plan of houses is geometrical and nearly symmetrical. Most of the adobe buildings in the city of Yazd had been vaulted with adobe roofs. Most of the studied vaults have segmental shape and only a few of them have pointed shapes so the latter were not considered due to their reduced representativeness. Different constructive solutions can be found over the vaults. In order to create the flat roofs in vaulted architecture, the space above the vaults can be fully filled with soil or present spandrel walls with small vaults on top, made of adobes, which is named “konou” in Persian architectural literature. Different constructive solutions over the vaults are illustrated in Fig 1. In order to better understand vaulted adobe houses of Yazd, vaults of “Talar” were chosen for a detailed geometric study. Aiming at assessing the in-plane behaviour of critical elevation of studied houses, the elevations consisting of “Talar” and its adjacency have been selected for further studies.

Figure 1. Different types of fill over the adobe vaults: (a) vault without fill, (b) vault full of soil, (c) spandrel walls and vaults over the main vault (“konou”).
2.1 Typological characterization of vaulted structures
In order to provide a more detailed geometrical analysis, vaults of “Talar” were chosen due to its presence in most of the traditional houses of Yazd. These vaults have the largest span among all the house’s vaults. From the carefully analysis of the “Talar” elevation view of each of the constructions present in the sample under study, it was possible to derive eight major typical configurations, as schematically shown in Fig 2, and organized according to the number of stories and the number and arrangement of vaults.

![Typologies for vaulted adobe structures](image)

Figure 2. Typologies adopted for vaulted adobe structures.

One-story vaulted constructions, classified here as typology T1.\(n\), represent about 45% of the sample, while 55% of the studied adobe houses have two stories or at least one part of the house consists of two floors (T2.\(n\)). For the sake of simplicity in geometrical and numerical studies, adjacent vaults have been considered fully parallel to the main vault and it was also assumed that existing thick adobe walls, staircases, perpendicular vaults or domes provide very stiff boundary conditions at each side. According to a statistical analysis carried out about the elevation view typologies, typologies T1.1 and T2.1 are clearly dominant in the sample, with 24% and 40% of elevation views; see Fig 3(a). These results allow to consider typology T2.1 as the most representative one, thus further studies will considered it in first place. Fig 3(b) illustrates the dominant typology of elevation view, T2.1, which is a combination of five vaults and supporting walls.
2.2 Reference vaults combination

The relation between span $s_1$ and rise to span ratio $r_1/s_1$ of the main vaults ("Talar" vault) is depicted in Fig 4 for one-story and two-story structures, respectively. The main vaults of reference vaults combination are also represented. Also, a proposal is done to classify the combinations of vaults into three main groups based on the span length of their main vault as follows:

- **Short span vaults** $s_1 \leq 5m$
- **Medium span vaults** $5m < s_1 < 6.5m$
- **Large span vaults** $s_1 > 6.5m$

According to the results obtained, it is concluded that 59% of the main vaults are classified as medium span vaults, 15% as short span and 26% as large span vaults. In order to study each group of vaults, it is convenient to define reference vaults combination as representatives of each group established above. The majority of short span vaults belong to one-story houses, while most of the large span vaults pertain to two-story houses or two-story part of the houses. Medium span vaults exist in both one-story and two-story constructions. Based on the statistical study of the sample, it can be stated that the two-story medium span group (MS2) constitutes a considerable proportion (33%) of the sample, thus it has been chosen here for further studies.

Figure 4. Relationship between span ($s_1$) and rise to span ratio ($r_1/s_1$) for the main vault (Talar): (a) one-story structures; (b) two-story structures.
Table 1 presents the geometrical features of the reference vaults of all the four groups considered. Parameter influencing structural response, such as effective vault thickness, is not measurable due to the existence of mud or gypsum plaster which covers the adobe vault. In addition the value of adobe vault thickness was not available in the literature survey. Therefore, in order to characterize the vault thickness, some of the half-ruined adobe vaulted houses were investigated and finally conservative values have been adopted for each group of vaults.

Table 1: Geometrical features of references of the vaults combination groups.

<table>
<thead>
<tr>
<th>Groups</th>
<th>s_1</th>
<th>r_1</th>
<th>h_1</th>
<th>r_2</th>
<th>h_2</th>
<th>w</th>
<th>s_2</th>
<th>r_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short span (SS1)</td>
<td>4.60</td>
<td>1.20</td>
<td>3.26</td>
<td>0.20</td>
<td>0.10</td>
<td>0.80</td>
<td>1.7</td>
<td>0.35</td>
</tr>
<tr>
<td>One-story (MS1)</td>
<td>5.70</td>
<td>1.30</td>
<td>3.10</td>
<td>0.25</td>
<td>0.10</td>
<td>0.84</td>
<td>1.6</td>
<td>2.34</td>
</tr>
<tr>
<td>Two-story (MS2)</td>
<td>5.70</td>
<td>1.30</td>
<td>4.30</td>
<td>0.25</td>
<td>0.10</td>
<td>0.84</td>
<td>1.9</td>
<td>1.98</td>
</tr>
<tr>
<td>Large span (LS2)</td>
<td>7.20</td>
<td>1.75</td>
<td>4.40</td>
<td>0.30</td>
<td>0.10</td>
<td>0.97</td>
<td>2.7</td>
<td>0.52</td>
</tr>
</tbody>
</table>

3. Numerical analysis of vaulted structures

Seismic safety of adobe vaulted architecture should be evaluated to distinguish the need and also the degree of possible intervention. The numerical safety assessment of historical masonry structures requires practical computational tools. Therefore it can be claimed that advanced non-linear analysis or other sophisticated models are more suitable for the assessment of remarkable monuments because they are very time and cost consuming, while simplified approaches like limit analysis are more appropriate for smaller buildings [18]. To this end, a numerical study using limit analysis theory implemented in Block2D software [17] has been performed to assess the seismic behavior of vaulted constructions. The vaults are assumed as assemblages of rigid blocks interacting through frictional interfaces for which calculations are carried out by means of the Block2D software, able to analyze the models under gravity and horizontal loading (earthquake load). The main result is a safety factor indicating the ratio between the collapse load and the structure weight [17, 19]. The collapse mode is also given.

As material properties, it was assumed a compressive strength equal to 1120 kN/m² [6], volume weight equal to 17.5 kN/m³ [6] and friction coefficient equal to 0.62 [20]. According to the geometrical study of case studies, reference vaults combination MS2 as the dominant typology has been chosen. In order to gain a better understanding of structural behaviour of the reference vaults combination, three types of fill cases were considered under both vertical and horizontal loading.

Table 2 presents the load factors reached. A given load factor represents the multiple of the initial load applied that causes structural failure. Results indicate that load factors of vaults combination without fill are the lowest and vaults combination with “konou” has the highest vertical and horizontal load factors. Fig 5 illustrates the failure mechanisms of reference vaults combination with “konou”, under vertical and horizontal loading. Both mechanisms show global failure, involving mainly the central vault and the adjacent walls.
Table 2: Vertical and horizontal load factors of reference vaults combination (MS2) with different types of fill.

<table>
<thead>
<tr>
<th></th>
<th>Without fill</th>
<th>Full fill</th>
<th>&quot;konou&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under gravity load</td>
<td>2.20</td>
<td>5.26</td>
<td>6.05</td>
</tr>
<tr>
<td>Under horizontal load</td>
<td>0.06</td>
<td>0.19</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Figure 5. Failure mechanism of reference vaults combination (MS2): (a) under vertical loading; (b) under horizontal loading.

3.1 Parametric analysis

The parametric analyses were performed to reach a profound understanding of the most effective parameters on the structural response of vaults combinations. There are variables that influence the structural safety such as main vaults span and rise, adjacent vault span, supporting walls thickness and also compressive strength of adobe. The relevant variables considered within this current parametric study and the corresponding adopted values for each variable are provided in Table 3. For parametric analyses of reference vaults combination, the “konou” option was chosen as this fill type is predominant in the vernacular adobe houses of Yazd.

Load factors of vaults combination with variable properties have been obtained considering both vertical and horizontal loading, as described above.

3.1.1 Vertical loading

The results of parametric analyses of vaults combinations under gravity load are illustrated in Fig 6. Increasing the span of main vault in the case of constant rise (main vault rise = 1.3 m) leads to reduction in vertical load factors of vaults combinations. Based on the obtained results, it can be claimed that vaults combinations have a higher vertical load factor when...
their main vault has higher rise. Geometrical properties of adjacent vaults influence the structural behaviour of the structure. When two vaults converge in a wall, the horizontal components of the thrust are neutralized in the case of identical vaults [21]. In this current study, increasing the span of adjacent vaults helps the whole structure to improve its equilibrium and thus increases the vertical load factor. Thickness of walls is also one of the effective parameters on the improvement of the structural load factor under vertical loading. Fig 6(c) shows that the variation of compressive strength of adobe considerably affects the safety of adobe vaults combination under vertical loading.

Figure 6. Relationship between vertical load factor and: (a) main vault span ($s_1$); (b) main vault rise ($r_1$); (c) adjacent vault span ($s_2$); (d) wall thickness ($w$); (e) compressive strength of adobe ($f_c$).

### 3.1.2 Horizontal loading

Fig 7 illustrates the results of parametric analyses of vaults combination under horizontal loading. Assuming a constant value for the rise, increasing the span of vaults causes reduction in the load factor values. The existence of main vaults with higher rise leads to an improvement of the horizontal load factor value of the whole structure. Also, increasing the adjacent vaults span slightly changes the horizontal load factor of vaults combination. After a small reduction, no changes were observed neither in load factor values nor on failure modes. The results from the analyses of vaults combinations with different walls thickness indicate that increasing the thickness of walls first increase the horizontal load factor of structure, but then no changes are observed. This fact shows that the wall thickness of about 0.95m is efficient for placing the trust line inside the wall and further increases of the wall thickness cannot improve the structural safety. According to the parametric analyses results, graph of
compressive strength of adobe versus horizontal load factors of vaults combinations displays ascending order.

Figure 7. Relationship between horizontal load factor and: (a) main vault span ($s_1$); (b) main vault rise ($r_1$); (c) adjacent vault span ($s_2$); (d) wall thickness ($W$); (e) compressive strength of adobe ($f_c$).

### 3.2 Discussion

The parametric study results indicate that under vertical loading a larger variation of load capacity has been observed when compared to the horizontal loading. Fig 8 illustrates a non-dimensional relationship between loads factors and studied variables. The most influencing parameter under the vertical load is main vault span. Main vault rise, compressive strength of adobe, wall thickness and adjacent vault span are the parameters that influence the structural behaviour of adobe vaults under gravity loads in decreasing order of importance. On the other hand, the variation in main vault span also affects the horizontal loads factor (e.g. during an earthquake) more than other parameters studied. Other parameters such as, main vault rise, wall thickness, compressive strength of adobe and adjacent vault span have influence on the seismic behaviour of adobe vaults in decreasing order of importance.

### 4. Main conclusions

In this paper, 60 traditional adobe vaulted vernacular buildings located in Yazd, Iran, were considered. A numerical parametric analysis using limit analysis approach was performed on a reference vault derived from a detailed geometrical study. A representative reference vault combination was analyzed under vertical and horizontal loads to evaluate its structural performance. The parametric analysis was performed to recognize the influence of important
parameters such as geometry and mechanical properties of materials on the structural safety of adobe vaulted structures.

For the studied adobe vaults combination, the vertical load factor obtained is always higher than one, indicating their safety under gravitational loads. However, horizontal load factors of all vaults combinations are less than 0.25g (i.e. the PGA value at Yazd), so most of the adobe vaulted structures under study may be not safe for a future earthquake in the area.

Finally this work shows that studying the effect of influential parameters on adobe vaults combinations can provide a deep insight into the safety and stability of traditional adobe vaulted houses, which may be at risk.

![Figure 8](image.jpg)

Figure 8. Non-dimensional relationship between variables and loads factors: (a) vertical loading; (b) horizontal loading (A: Main vault span, B: Main vault rise, C: Wall thickness, D: Adjacent vault span, E: Compressive strength of adobe).

Acknowledgments

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ASSESSMENT OF THE INJECTION OF GROUTS TO REPAIR CRACKS IN RAMMED EARTH

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Abstract
Rammed earth constructions are known for their high seismic vulnerability, which menaces their preservation and puts in risk the life of millions of people living in regions with important seismic hazard. The poor conservation condition of many of these constructions largely contributes for the aforementioned situation. The presence of cracks is one common type of damage occurring in the walls, which debilitates their structural behaviour both for in-plane and out-of-plane loading. The injection of grouts has been studied recently as a solution to repair this type of damage. However, the repair effectiveness of this technique needs further research. This paper presents an experimental program, where the effectiveness of the injection of a mud and a commercial grout base on hydraulic lime for repairing cracks in rammed earth is compared. Diagonal compression test were carried out on wallets before and after repair, where the response was monitored with Digital Image Correlation (DIC). Furthermore, sonic tests were used as a technique to assess the repair efficiency by non-destructive means. In general, both types of grouts presented similar performance.

1. Introduction

Even nowadays, building with raw earth is a popular solution to build shelter in developing countries. On the other hand, earth construction represents an almost negligible percentage of the new construction in developed countries. Despite that, an important earth built stock exists spread around the World [1], where it was estimated that in 1983 one third of the World’s population was living in [2]. Among this built stock, exists several buildings and sites with important heritage value, such as Chan-Chan (Peru), the Great Wall of China (China), the Alhambra (Spain), the old town of Ghadames (Libya), the Ksar of Ait-Ben-Haddou (Morocco) and the Old Walled City of Shibam (Yemen), classified as World Heritage [3].
The concept of earth construction involves several techniques, since it is also related with the concept of vernacular architecture [4], where the local construction of the populations is shaped according to local factors. These factors include available building materials, local weather, as well as cultural, social and economic aspects of the population. Among the earth construction techniques, rammed earth constitutes one of the most popular, along with adobe masonry [5]. Building in rammed earth consists in compacting moist earth by layers inside a removable formwork to build monolithic walls. The use of a formwork and the ramming process constitute key features that differentiate this technique from other earth construction techniques. The construction process is carried out by courses (like masonry), where the formwork runs horizontally along the perimeter of the construction and then is lifted to build the next course [6].

Rammed earth constructions, like other earth construction techniques, are known for presenting high seismic vulnerability. This is a consequence of several factors, namely the low mechanical properties (especially the very low tensile strength), high dead-weight and poor connection between elements [7]. Taking into attention the fact that most of the earth constructions are built on regions with important seismic hazard, it becomes evident the urgent need in promoting the seismic retrofitting of the existing rammed earth built heritage.

In Southern Portugal, namely in Alentejo and Algarve, exists a significant rammed earth built stock, where are included military and civil constructions [8]. The first ones are mainly constituted by, still existing, millenary fortifications built during the Islamic presence in the Iberian Peninsula between the 8th and 13th centuries, such as Paderne’s Castle [9]. The second ones are mainly constituted by dwellings built before the nineteen fifties, where a significant part of the population still lives in. However, Alentejo and Algarve are regions that present unneglectable seismic hazard, which combined with the seismic vulnerability of these constructions, puts in risks the preservation of this heritage and the life of their inhabitants. Furthermore, many of the rammed earth constructions in the region are found in poor conservation condition, which contributes for increasing the seismic vulnerability of these constructions [10]. The presence of cracks is among the most common types of damage often found in rammed earth walls, which has particular influence on the global structural performance. Cracks constitute preferential paths for rainfall infiltration, which are responsible for moistening directly the rammed earth, which reduces substantially its mechanical properties [11]. Structural cracks in rammed earth walls decrease their bearing capacity and stiffness, and disrupts the overall monolithic behaviour of the structure.

The adequate repair of rammed earth walls is required to re-establish the original structural behaviour of the whole structure, which needs to be complemented further with strengthening measures to improve the seismic safety. Cracks can be repaired using different techniques, but whose efficiency greatly varies from case to case [12]. For instance, the most basic solution consists in simply filling the crack with earth mortar, but the limited space and consistency of the mortar are major limitations to guarantee complete filling. Furthermore, earth mortars tend to crack due to exaggerated drying shrinkage, which limits the establishment of the bond disrupted by the filled crack.
The injection of grouts has been recently studied for repairing cracks [13], where the grout consists of a sufficiently fluid mortar capable of filling completely the crack. One of the premises of the research carried out by Silva [13] consists in the development of compatible grouts, which included earth in their composition and therefore are called mud grouts. The development and use of these grouts has been based on recommendations of a technical committee designated by the Getty Conservation Institute on earth construction [14]. Diagonal compression tests carried out on rammed earth wallets repaired with the developed mud grouts have shown that the injection repair promoted satisfactory shear strength recovery of the specimens, but was ineffective in recovering the initial shear stiffness.

On the other hand, the preparation of a mud grout is not an easy task, since it requires sieving the fine particles of the soil, which make the whole process very expensive. Despite being assumed that the compatibility of hydraulic lime based grouts is inferior to that of mud grouts, the first grouts are easily found in the market with affordable cost. Taking this into account, this paper aims at comparing the effectiveness of a mud grout with that of a commercial hydraulic lime based grout for repairing cracks in rammed earth. An experimental program was prepared with this respect, where rammed earth wallets were tested under diagonal compression, and then retested after injection repair. The tests took advantage of the digital image correlation (DIC) technique, which constitutes a valid procedure to the derivation of the full field surface displacements and strains of objects under load. The technique is based on the comparison of two digital images of the object, before and after deformation [15]. In addition, the experimental program also aimed at evaluating the used of sonic tests for assessing the effectiveness of the injection repair by non-destructive means.

2. Experimental program

The repair effectiveness of the injection repair of cracks in rammed earth walls was assessed by means of diagonal compression tests carried out on wallets representative of unstabilised rammed earth from Alentejo. First, the wallets were built in laboratory and were tested after drying. After testing, they were repaired with grout injection and retested. Sonic tests were also used before the first and second tests in order to evaluate the capacity of this method for assessing the repair effectiveness by non-destructive means.

2.1 Rammed earth specimens

Six wallets were built using soil collected from Amoreiras-Gare (Alentejo, Portugal), whose particle size distribution was corrected in advance, in the proportions 50% of soil, 28% of river sand and 22% of gravel. The corrected soil presented percentages of clay, silt, sand and gravel of about 14%, 16%, 32% and 37%, respectively. The wallets presented as dimensions 550x550x200 mm³ and were compacted in nine layers with similar thickness. The density of the layers was controlled taking into account the maximum density obtained from the standard Proctor test, while the water content for compaction was controlled by means of the drop ball test [16]. In addition, six cylindrical specimens were also compacted with 100 mm diameter and 200 mm height. These cylinders were used to evaluate the compressive strength and Young’s modulus of the rammed earth, whose average values were of about 1.5 N/mm² and 536 N/mm², respectively. Further information on the construction of the specimens is detailed elsewhere [17].
2.2 Testing procedure

The diagonal compression tests of the wallets were carried out according to the procedure of ASTM E 519 [18]. The test setup is depicted in Figure 1, where it is illustrated that the deformations of the specimens were measured by means of LVDTs attached to the middle third of each diagonal in one of the faces. The other face was used for DIC photographs, and was painted white for then creating a random black spot pattern to facilitate the DIC analysis. The shoes used to support the wallets and applying the load were made of steel, with a width of about 100 mm. The contact with the specimens was rectified by means of neoprene rubbers introduced between specimens and shoes. The load was applied under monotonic displacement control at rate of $2 \mu m/s$. This procedure was used in first and second tests of each wallet, where the second test was carried out about 28 days after the repair.

![Figure 1](image)

Figure 1. Setup of the diagonal compression tests: (a) face with deformations measured with LVDTs; (b) face used for DIC analysis.

2.3 Repair procedure

The failure of the wallets resulted in the division of the specimens in some parts, which were removed from the testing apparatus and remounted together. The cracks were sealed using an earth mortar prepared with soil used to build the walls, sieved to remove the particles larger than 4.75 mm (see Figure 2a). Simultaneously, injection tubes with 6 mm diameter and made of flexible plastic were installed in one of the sides of the specimens. The tubes were positioned in such way that they would penetrate about 4 cm in the wallets, and that the maximum space between injection tubes would be of about 10 cm. The injection was carried out after letting the sealing mortar harden completely. With this respect, a syringe with 100 ml capacity was used to inject water in all injection tubes, 1 hour before injecting the grouts. This procedure aimed at mitigating the water sorption of the grouts, promoted by the rammed earth. The injection started from the bottom tubes up to the top ones, using the same syringe aforementioned (see Figure 2b). The injection of each tube stopped when the grout leaked from the next tube. Then, the injection tube was sealed and the injection was continued from the leaking tube, and so on.

As referred previously, two grouts were used to repair three wallets each, namely grout NMG40-60 and FB 790. NMG40-60 constitutes a mud grout composed by the same soil used to build the rammed earth wallets (S#80). The soil was wet sieved to remove the particles larger than 0.180 mm, which was defined as the maximum particle size of the mud grout. Limestone powder (200-OU) was also included in the composition as filler material, aiming at leaning the
clay content of the sieved soil. The clay content of the mud grout is estimated to be of about 21%. Sodium hexametaphosphate (HMP) was also used with the objective of providing adequate fluidity to the grout, while keeping the water/solids ratio (W/S) low. FB 790 is a commercial grout based on hydraulic lime and is provided by Fassa Bortolo. This grout is specially indicated, by the manufacturer, for consolidation of historical masonry. The composition of the grouts is summarized in Table 1, where it should be noted that tap water was used for both cases.

![Figure 2. Repair of the wallets: (a) sealing of the cracks and installation of the injection tubes; (b) injection of the mud grout.](image)

Table 1: Composition of the grouts.

<table>
<thead>
<tr>
<th>Grout</th>
<th>S#80 (wt.%)</th>
<th>200-OU (wt.%)</th>
<th>HMP (wt.%)</th>
<th>FB 790 (wt.%)</th>
<th>W/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMG40-60</td>
<td>40</td>
<td>60</td>
<td>0.46</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>FB 790</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 2 presents the properties of the grouts in terms of flow time of 1 dm³ (according to ASTM C 939 [19]), average flexural strength ($f_b$) and average compressive strength ($f_c$) (according to EN 1015-11 [20]). The low W/S ratios of both grouts are similar and resulted in very similar flow time values. This seems to mean that a mud grout can achieve similar fluidity to that of a commercial one, while keeping similar W/S ratios. With respect to the strength values, the mud grout is 60% weaker than FB 790. This difference can be even higher at long-term with the hardening of the binder, since FB 790 was tested with 28 days of age. Despite of the Young’s modulus of the grout FB 790 not being measured, such high values of strength, with respect to the rammed earth, indicate that the mechanical compatibility between both materials might be compromised.

Table 2: Properties of the grouts.

<table>
<thead>
<tr>
<th>Grout</th>
<th>Flow time (s)</th>
<th>$f_b$ (N/mm²)</th>
<th>$f_c$ (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMG40-60</td>
<td>42.3</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>FB 790</td>
<td>43.9</td>
<td>3.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>
2.4 Sonic tests
Sonic tests were used to evaluate the effectiveness of the repair procedure of the tested rammed earth wallets, by measuring the homogeneity of the material before and after the injection of the grout. Sonic tests are Non Destructive Tests (NDT) that consist in transmitting stress waves within the frequency range of acoustic waves (20 Hz to 20 kHz), generated by an instrumented hammer, and in measuring their travel time through a section of the material by means of accelerometers. The set of instruments used to measure and analyze the signal consists of an instrumented hammer for the initial pulse; a piezoelectric accelerometer that measures the generated signal; an acquisition unit from National Instruments; and a computer with the software for acquisition, visualization and analysis of the results (Figure 3a). Direct tests were performed along the length of the wallets, from edge to edge, in 3 points of measurement with a distance of 55 cm. Indirect tests were performed in both sides using a grid of 3 by 3 points with a distance between points of measurement of about 35 cm (Figure 3b). The total number of points was 15 for each panel, with 15 measurements per point. From each point, the 6 most representative signals were evaluated, and only those with a coefficient of variation lower than 20% were considered for the analysis of the results.

3. Results and discussion
The results of the diagonal compression tests and sonic tests performed on the rammed earth wallets before and after repair are here presented and discussed.

3.1 Diagonal compression tests
Table 3 and Table 4 summarize the results of the diagonal compression tests carried out on the wallets repaired with grout NMG40-60 and FB 790, respectively. These tables include the dry density of the wallets \( \rho_d \), shear strength \( f_s \) and shear modulus \( G_0 \) before injection, shear strength \( f_{sg} \) and shear modulus \( G_{0g} \) after injection. The shear moduli were computed between 5% and 30% of the shear strength of the respective specimen. Figure 4 presents the shear stress – shear strain curves of the specimens before and after repair. In general terms, the curves of the first test are characterized by an early peak shear stress, which is followed by a marked stiffness loss. This early peak shear stress is thought to be related with the loss of cohesion (i.e. to the binding capacity) promoted by the clay fraction, as reported previously by Silva [13]. The shear behaviour of the wallets up to this peak seems to result from the contribution of the clay fraction to cohesion, and friction and interlocking capacity of the gravel-size (or larger) aggregates. Hereafter, the behaviour relies only on the friction and
interlocking. The wallets also presented a large shear deformation capacity, which seems to be a feature that is expected to contribute to energy dissipation during a seismic event.

Table 3: Results of the diagonal compression tests carried on the specimens repaired with grout NMG40-60.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\rho_d$ (g/cm³)</th>
<th>$f_{si}$ (N/mm²)</th>
<th>$f_{sg}$ (N/mm²)</th>
<th>$G_{0i}$ (N/mm²)</th>
<th>$G_{0g}$ (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIWURE_1</td>
<td>2.05</td>
<td>0.12</td>
<td>0.05</td>
<td>1056</td>
<td>14</td>
</tr>
<tr>
<td>IIWURE_3</td>
<td>2.04</td>
<td>0.17</td>
<td>0.08</td>
<td>632</td>
<td>20</td>
</tr>
<tr>
<td>IIWURE_4</td>
<td>2.04</td>
<td>0.13</td>
<td>0.07</td>
<td>1068</td>
<td>8</td>
</tr>
<tr>
<td><strong>Average (CoV)</strong></td>
<td><strong>2.04 (1%)</strong></td>
<td><strong>0.14 (14%)</strong></td>
<td><strong>0.06 (18%)</strong></td>
<td><strong>919 (22%)</strong></td>
<td><strong>14 (36%)</strong></td>
</tr>
</tbody>
</table>

Table 4: Results of the diagonal compression tests carried on the specimens repaired with grout FB 790.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\rho_d$ (g/cm³)</th>
<th>$f_{si}$ (N/mm²)</th>
<th>$f_{sg}$ (N/mm²)</th>
<th>$G_{0i}$ (N/mm²)</th>
<th>$G_{0g}$ (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIWURE_2</td>
<td>2.04</td>
<td>0.16</td>
<td>0.07</td>
<td>1356</td>
<td>99</td>
</tr>
<tr>
<td>IIWURE_5</td>
<td>2.05</td>
<td>0.13</td>
<td>0.07</td>
<td>460</td>
<td>22</td>
</tr>
<tr>
<td>IIWURE_6</td>
<td>2.05</td>
<td>0.12</td>
<td>0.07</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td><strong>Average (CoV)</strong></td>
<td><strong>2.05 (1%)</strong></td>
<td><strong>0.14 (14%)</strong></td>
<td><strong>0.07 (2%)</strong></td>
<td><strong>908 (-)</strong></td>
<td><strong>51 (66%)</strong></td>
</tr>
</tbody>
</table>

The wallets injected with the grout NMG40-60 showed shear strength values in the range of 0.05 and 0.08 N/mm² with an average value of 0.06 N/mm², while the wallets injected with FB 790 showed values of about 0.07 N/mm². In average, it was possible to recover about 44% and 51% of the initial shear bearing capacity for grout NMG40-60 and FB790, respectively. Both rates of repair effectiveness are similar, which seems to show that a commercial grout may have similar performance to that of a mud grout. It should be noted that, similar values of repair effectiveness were reported by Silva [13]. Furthermore, it was again observed the incapability of the grout injection in recovering the initial shear stiffness, confirming the inefficiency of this technique in recovering the friction and interlocking effect of the coarse particles, even that a stiffer grout (FB 790) is used. In fact, grout FB 970 presented higher shear stiffness recovery (about 3 times) than that of grout NMG40-60. Still, the values of the shear stiffness after repair are marginal when compared with the initial shear stiffness.

Figure 5 presents the maximum principal strains obtained from DIC analysis for wallets IIWURE_4 (grout NMG40-60) and IIWURE_2 (grout FB 790) in the first and second tests. These images were obtained, for each test, in a near collapse stage of the wallets. Despite the DIC analysis being resumed to this stage, it allowed to follow the development of the strain field of the specimens during the tests. In general, the failure of the wallets in the first test is characterized by the formation of a main crack or set of cracks with diagonal orientation that cross the entire specimen. The formation of these cracks occurs suddenly at the middle of
specimens just before the peak load, and then progresses towards the supports. Cracks at the interfaces between layers are also formed, where the interfaces of IIWURE_4 seem to be weaker than those of IIWURE_2. With respect to the second test, the development of the diagonal crack was progressive since the beginning of the test. For all repaired wallets, the development of the main crack seems to occur in some regions coincident with the original crack. This situation occurs do to the fact that the rammed earth is damaged in the region adjacent to the crack and not because any of the grouts present little adhesion capacity. In fact, the inspection of the wallets after testing as shown a good adhesion of both grouts, since failure occurred mostly by the rammed earth.

Figure 4. Shear stress-strain curves of the wallets in the first and second tests: (a) grout NMG40-60; (b) grout FB 790.

Figure 5. Maximum principal strains (near collapse stage) obtained from DIC analysis for IIWURE_4 and IIWURE_2 in the first and second tests.
3.2 Sonic tests

The results of the direct and indirect sonic tests carried out on the wallets are presented in Figure 6. The direct tests before the first test of the wallets resulted in an average P-wave velocity value of about 2469 m/s, which is comparable to those of a mid-good quality masonry. This value was reduced in about 18% in the repaired wallets, which confirms the loss of homogeneity of the material. This situation can be explained by the presence of damage in the rammed earth, which could not be repaired. The use of different types of grouts seems not to affect the results, as they were very similar for both grouts used. Similar observations can be drawn from the indirect tests, where the average value of the R-wave velocity before the first test was of about 963 m/s, which decreased about 17% with respect to the repaired wallets. It should be noted that the measurements of the sonic tests are expected to be affected by the sealing mortar on the faces of the wallets, which can penetrate up to 2 cm inside. This material has obviously lower properties than the rammed earth and grout and therefore it tends to slow down the propagation of the sonic waves. In this way, it is difficult to conclude about the reliability of sonic tests in assessing the repair effectiveness of grout injection to repair cracks in rammed earth.

![Figure 6. Results of the sonic tests: (a) direct tests; (b) indirect test.](image)

4. Conclusions

The experimental program presented in this paper allowed to confirm some aspects regarding the shear behaviour of rammed earth and the repair effectiveness of mud grouts, as reported by Silva [13]. In addition, it was observed that the repair effectiveness of a commercial grout based on hydraulic lime seems to have a similar repair effectiveness to that of a mud grout. Despite the good performance of this grout, its use should always take into account other compatibility issues, not discussed here. Finally, sonic tests seem not to be a reliable method to assess the repair effectiveness of injection by non-destructive means.

Acknowledgments

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References

EXPERIMENTAL STUDY OF BRICK MASONRY WALLS SUBJECTED TO ECCENTRIC AND AXIAL LOAD

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(1) Universitat Politecnica de Catalunya · BarcelonaTech, Spain

Abstract
Masonry buildings represent a huge building stock. The need for preservation of masonry structures may be due to various reasons: economic, heritage, etc. These buildings are often subjected to diagnosis processes that involve structural assessment which can be complex when the slenderness of the walls and the eccentric loading are taken into account. Load-bearing masonry walls have a complex structural response characterized by the second-order bending effects often caused by the eccentricity of the load. This characteristic is taken into consideration in the Spanish and European regulations which contemplate decreases in the bearing capacity of the walls according to their slenderness. This contrasts with the actual behaviour of the walls, since the collapse rarely occurs due to buckling.

This paper presents the results of an experimental campaign that has been carried out in order to study the effects of slenderness and axial and eccentric load in structural masonry walls. For this purpose, masonry walls with different mortar dosages and identical type of moulded bricks have been tested under different load conditions. The results of the tests are compared to those given by the current regulations, European and Spanish, EUROCODE-6 and CTE.

Keywords: Brick masonry walls, wall testing, buckling

1. Introduction
Looking back in history, it can be ratified that many of the historic buildings in Catalonia and the rest of Spain have been built with masonry structures, especially brick masonry structures. This has been the most common solution until the first half of the XXth century when steel and concrete structures have become usual in construction.
Masonry buildings in this historical build stock are often subjected to diagnosis processes that involve structural assessment which can be complex due to the difficulties in establishing its safety conditions.

Spanish and European regulations [1] [2] take into consideration the complex behaviour of the masonry, contemplating decreases in the load bearing capacity of the walls according to their slenderness. It is considered that when a compression load (centred or not) is applied to a slender masonry element, it will end up collapsing due to the excessive stress that concentrates in one part of the section as a result of buckling. This fact contrasts with the actual behaviour of the structural walls in such buildings, since scarce damage is observed due to buckling and actual slender walls reach tensions far above the regulation limits [3].

This paper presents the results of an experimental campaign that has been carried out in order to study the effects of slenderness and axial and eccentric load in structural masonry walls.

2. Aims and purpose

The main objective of the present paper is to obtain data of the compression stresses that reach load bearing slender walls at real scale to analyse the effect of buckling on the section of masonry when simple and eccentric compression are applied. The resulting data provide information that may help in the diagnosis of historical brick masonry buildings.

3. Methodology

3.1 Test design

The experimental campaign was based on 12 tests on 12 slender wall specimens. In order to obtain behaviour as close to the reality of such historic buildings, the wall specimens were real size: 13.5cm thick, corresponding to the actual thickness of the so-called Catalan brick, 87.5cm wide and 300cm high. With that aim, bricks, brickwork and mortar dosages were carefully chosen. Mortars used in the wall tests were portland cement CEM II / B-P 32.5 with river sand exclusively, their dosages were low: 1:6 and 1:9. In Table 1 mortar dosages used in each of the tests are specified. Bricks used in the wall test building were ceramic manual moulded bricks which reach state regulations requirements [4].

Bricks, mortars and masonry were characterized. Compressive strength tests were carried out in each of them according to regulations [5][6] and [7] respectively. Results are shown in table 2.

In order that the lower end of the wall specimens behave as similar as possible to the actual bonding conditions of walls in masonry structure buildings, each of the walls was built on a UPN160 profile which was filled with a non-retraction mortar Bettogroud 150. Consequently, the connection between the wall and the floor results not a ball joint but a support without lateral rotation possibilities.
Table 1: Wall tests references and main characteristics

<table>
<thead>
<tr>
<th>Test Reference</th>
<th>Mortar dosages</th>
<th>Width of joining (cm)</th>
<th>Dimensions (cm)</th>
<th>Upper ending</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:6</td>
</tr>
<tr>
<td>3</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:6</td>
</tr>
<tr>
<td>4</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:6</td>
</tr>
<tr>
<td>5</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:6</td>
</tr>
<tr>
<td>6</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:6</td>
</tr>
<tr>
<td>1.1</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 295</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>7</td>
<td>1 : 9</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>8</td>
<td>1 : 9</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>9</td>
<td>1 : 9</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>10</td>
<td>1 : 9</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>11</td>
<td>1 : 9</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>12</td>
<td>1 : 9</td>
<td>1</td>
<td>13.5 x 87.5 x 300</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>4R</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 276.5</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
<tr>
<td>5R</td>
<td>1 : 6</td>
<td>1</td>
<td>13.5 x 87.5 x 280</td>
<td>C.P. 1:3 (15% C.A.C.)</td>
</tr>
</tbody>
</table>

Table 2: Wall materials characteristics

<table>
<thead>
<tr>
<th>w/c</th>
<th>Compressive strength (28 days) N/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mortar 1:6</td>
<td>0.99</td>
</tr>
<tr>
<td>Mortar 1:9</td>
<td>1.37</td>
</tr>
<tr>
<td>Bricks</td>
<td>27.4 ± 1.2</td>
</tr>
<tr>
<td>Brick masonry 1:6</td>
<td>12.2 ± 0.7</td>
</tr>
<tr>
<td>Brick masonry 1:9</td>
<td>11.3 ± 0.8</td>
</tr>
</tbody>
</table>

During the execution, the verticality of the wall specimens was taken thoroughly; also, the masonry joint measure was fixed in 1 cm, controlling the consistency of the mortar according to the current regulations [8]. Two UPN100 profiles were fixed in each face of each wall to ease the placing of the wall specimens under the press machine.

The upper end of the walls was made by two different mortars. The first round of tests had an upper ending made of portland cement mortar 1:6 while the second round had a portland cement mortar ending 1:3 with 15 % of aluminous cement (calcium aluminate cement). The second ending solution was held because the mortar setting was faster.

3.2 Compressive test

The compressive test consisted on the application of an increasing load on the wall test specimens described in the preceding paragraphs. Load application has been carried out with a dynamic MTS press of 15MN to a constant displacement speed of the piston of the pressing machine of 0.5mm/min. Each test had two phases:
Phase 1: load application in stepwise increments of 0.1MN. Deformation measurements take place with a deformometer. During the whole sequence the instrumentation performs a continuous recording of the displacements. The sensor of the pressing machine also provides deformational data during the test.

Phase 2: once a certain load is reached, the instrumentation is removed and then a continuous load is applied until the wall specimen collapses.

The instrumentation of deformation of each sample has been threefold:

- Measurement of transversal deformation with LVDT displacement sensors (Figure 1) allowing real time displacement measurements. Sensor sensitivity is 0.01mm and the accuracy is above 0.5%.
- Placement of measuring points for deformometer readings on the front face of the wall specimen for measuring horizontal and vertical displacements (Figure 1). Accuracy sensitivity of the deformometer is 0.002mm.
- Height displacement measurement performed by the own pressing machine sensor.

In a first group of tests, the load transmission to the wall specimens is performed by the placement of a neoprene band between the ending mortar layer in contact with the pressing machine and the wall (Figure 2). This procedure was rejected, since once the load is applied; the failure appears in an unexpected way. In this first group, a vertical crack appears on the top of the wall as a result of the tensile stresses induced at this spot by the neoprene band. Afterwards, contact with the press was modified by applying the load through a UPN profile in contact with the press over a regularization mortar layer (Figure 2). This change is made to achieve a more realistic behaviour. The results provided in this paper correspond to those obtained with the second solution of transmission load.
Figure 1. Location of the LVDT sensors (left) and deformometer measuring points (right)

Figure 2. Load conditions on the different tests
4. Results

The results of the compressive tests are provided here below (table 3). It can be observed that the stresses reached are slightly higher in the walls where the load is centred. However, when considering the most common type of failure of the wall tests (Figure 3, Table 3), the cracking corresponds to a flexo-compression stress whether the load is centred or not. This fact is corroborated when the transversal deformation data provided by the LVDT sensors placed along the wall test specimens is observed (Figure 4).

Table 3: breaking stresses and deformation modules of the compressive tests.

<table>
<thead>
<tr>
<th>Wall</th>
<th>Breaking stress N/mm²</th>
<th>Deformation module N/mm²</th>
<th>Eccentricity (m)</th>
<th>Type of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>11.36</td>
<td>3070</td>
<td>0</td>
<td>Whole height length cracking and collapse</td>
</tr>
<tr>
<td>7</td>
<td>7.00</td>
<td>2450</td>
<td>0</td>
<td>Vertical cracking</td>
</tr>
<tr>
<td>8</td>
<td>8.94</td>
<td>2500</td>
<td>0.045</td>
<td>Vertical cracking and collapse</td>
</tr>
<tr>
<td>10</td>
<td>9.45</td>
<td>2834</td>
<td>0</td>
<td>Vertical cracking and collapse</td>
</tr>
<tr>
<td>11</td>
<td>8.33</td>
<td>2503</td>
<td>0.045</td>
<td>Vertical cracking and collapse</td>
</tr>
<tr>
<td>12</td>
<td>6.76</td>
<td>2470</td>
<td>0.042</td>
<td>Vertical cracking and collapse</td>
</tr>
<tr>
<td>4R</td>
<td>10.39</td>
<td>3124</td>
<td>0</td>
<td>Vertical cracking and collapse</td>
</tr>
<tr>
<td>5R</td>
<td>8.45</td>
<td>2618</td>
<td>0.045</td>
<td>Vertical cracking and collapse</td>
</tr>
</tbody>
</table>

Hereafter, the data obtained from the compressive tests is compared with the masonry compressive strength (table 1) considering the reduction of bearing capacity caused by slenderness in EUROCODE-6 [2]. Table 4 shows the reduction factor for slenderness and eccentricity f for each wall considering its characteristics and the eccentricity of the load application.

In the cases where the load is centred, the reduction in the load bearing capacity for slender walls given by the EUROCODE-6 [2] is smaller, so the theoretical compressive strength values are comparable to those obtained in the compression tests. However, in the cases where the load is eccentric such load bearing capacity reduction is significantly reduced. In this last case the results of the tests are above those theoretical values, this fact is discussed in the conclusion section.
Figure 3. Break of the test number 7, with centred load (left), and 1, with eccentric load (right).

Figure 4. Deformation results
5. Conclusions
Regarding the cracking of the tests, it has to be noted that although these have been carried out in slender walls no cracks have been observed due to buckling. However, in most cases (7 of 8), readings show small movements of destabilization in the central zone of the specimen. Leaving aside the cracks by local effects, mainly induced at the top of the wall by the charging system, it can be concluded that the maximum compressive load at the time of the main cracking reaches between 40 and 60% of the maximum load at the time of collapse.

The effect of the load eccentricity shows in practice a relatively small decrease in the load bearing capacity. This fact contrasts with the load bearing capacity reductions established by the current legislation which seems to be clearly designed for construction.

In existing building assessment multiple different inputs have to be taken into account in order to provide an accurate diagnosis.

6. References
Abstract
Volubilis is the largest archaeological site in Morocco. It has been registered on the UNESCO World Heritage list since December 1997. Its main building stone is a yellowish-beige calcarenite limestone, characterized by its heterogeneity. For preservation purposes, this study investigated correlations between the properties of calcarenite stone measured in the laboratory and two non-destructive tests, Karsten tube water absorption and Leeb hardness. Tests were carried out on samples of calcarenite stone extracted from the main original quarry. The results confirmed the variability of the quarry stone properties and showed that the Karsten tube test could be used to estimate capillary water absorption and determine directional dependence. They also showed that the square root of Karsten absorbed water was related to laboratory measurements of porosity and total water absorption by linear correlations. Moreover, hardness was linearly correlated with the porosity and density of the tested calcarenite stone.

1. Introduction
Volubilis is a remarkable archaeological site in Morocco that has been registered on the UNESCO World Heritage list since December 1997. It was a Mauritanian capital founded in the 3rd century B.C. and covers about 42 hectares. The main building stone at Volubilis is a yellowish-beige calcarenite limestone. It represents about 60% of the total volume of building stones and was extracted from the Ain Schkor quarry located within 5 km from the site [1]. This building stone is characterized by its heterogeneity and variability both in monuments and in the quarry. A major project to preserve the site was launched in 2015. As for any restoration intervention, diagnosis comprises in situ measurements and sampling of stones from monuments and the quarry to conduct laboratory tests. Sampling at the monument scale should be both representative and as limited as possible in order to respect the minimum
intervention principle [2] and avoid causing additional damage. Two non-destructive devices, Karsten tube and the Piccolo hardness tester, were therefore used with the aim of distinguishing dissimilar varieties of the calcarenite stone on the scale of monuments and selecting the most appropriate blocks within the original quarry to replace deteriorated stones. This study investigates the possibility of estimating physical properties of calcarenite stones such as bulk density, porosity, total water absorption and capillary absorption, from the two non-destructive tests.

2. Materials and methods

The tests were performed on 25 cubic samples of calcarenite limestone with 50 mm side length. They were prepared using a diamond saw, from blocks collected in the Ain Schkor quarry. Calcarenite stone is heterogeneous, porous and sandy in texture. It is mainly composed of calcite with a small proportion of quartz [1].

Porosity P(%), bulk density $\rho_b$ and solid matrix density $\rho_s$ were determined using the hydrostatic weighing method [3]. It is based on the determination of three masses: the mass of the sample in dry state, the mass of the sample in fully saturated state, and the mass of the sample in fully saturated state but immersed in water. The total water absorption test was conducted according to [4] under atmospheric pressure. The samples were dried until reaching a constant mass. They were then immersed in water for 48h. The water absorption $W(\%)$ was equal to the quotient of the increase in mass due to immersion and the dry mass.

The capillary water rise test was carried out on dried samples for the three directions by following the procedure described in [5]. Samples were placed in a basin of water in such a way that only the bottom of the sample (3+/-1mm) was in contact with water. The sample mass was periodically measured. The water absorption per contact unit area versus the square root of the time was then plotted. The slope of the first part of the curve corresponds to the capillary absorption coefficient $A$.

In addition to the previous tests, the water absorption of three perpendicular sides was measured using a Karsten tube. The test was repeated 3 times to check its repeatability by calculating the variation coefficient CV as the ratio of the standard deviation to the mean. A Karsten tube is a pipe-shaped glass tube graduated from 0 to 4 ml and divided into sub-gradations of 0.1 ml (Figure 1). It is sealed to the vertical surface of the stone by plastiline and filled with water until a zero reading is obtained. The water column has a height of 9.8 cm exerting a pressure of 961.38 Pa on the stone surface [6]. The amount of water absorbed during a period of time can be recorded by reading the drop in the water level. In order to compare this test to the standard capillary rise method, a similar capillary absorption coefficient $C_k$ was determined as previously without considering the absorbed water before 2 min. The surface of the cylindrical body sealed to the sample was taken equal to 5.7cm². Likewise, the volume of water absorbed between 2 min and 30 min ($W_{30-2}$) was determined.

In addition, hardness measurements were performed using a Piccolo 2 portable hardness tester, a compact version of the standard Equotip (Figure 1). It is an electronic rebound
hardness testing device with automatic compensation for impact directions other than vertical. During measurement an impact body with a hard metal ball indenter is launched by spring energy against the sample to be tested and then rebounds. The hardness value is defined as the ratio of the rebound velocity to the impact velocity multiplied by 1000 [7]. It is directly readable on a LCD and expressed as Leeb hardness (HL). For each sample, the single impact method was followed: 10 measurements were taken at 10 different points on each pair of parallel sides; their average value and variation coefficients were then calculated.

Figure 1. Devices used in this study: Karsten tube and Piccolo hardness tester

3. Results and discussion

3.1 Characterization results

The results of the laboratory characterization conducted on the calcarenite stone samples are summarized in Tab. 1. They show that the calcarenite stone exhibited significant ranges of physical properties. The porosity $P$ varied from 6.17 to 25.94 % with an average of 15.03 %, whereas the bulk density $\rho_b$ varied between 1.95 to 2.43 g/cm$^3$. The solid matrix density, which depends only on mineralogical composition, varied from 2.56 to 2.68 g/cm$^3$. These solid matrix densities are close to the densities of the main minerals in calcarenite stone: calcite (2.71 g/cm$^3$) and quartz (2.65 g/cm$^3$) [8]. The total water absorption $W$ ranged between 2.09 and 10.14 %, and was generally correlated to the porosity. The capillary water absorption coefficient $A$ showed a large range 0.37-5.86 kg/m²h$^{0.5}$ with an average of 1.98 kg/m²h$^{0.5}$. Consequently, according to the classification proposed in [9], 20 % of calcarenite samples are highly absorbing ($A > 3$ kg/m²h$^{0.5}$), 12 % are slightly absorbing samples ($A< 0.5$ kg/m²h$^{0.5}$) and 68 % are medium absorbing. As for the total water absorption, the higher the porosity, the higher the capillary water absorption. Moreover, the capillary water absorption exhibited a directional dependency as the anisotropy index ($\Delta (\%) = 100 \times (A_{\text{max}} - A_{\text{min}})/A_{\text{max}}$) varied between 5 and 75 % with an average of 34 %. Anisotropy values of more than 70 % are relatively common [10].

Tab. 2 lists the results of the Karsten tube and Piccolo hardness tests for the three directions (D1, D2 and D3). The calcarenite samples showed significant ranges of the water absorption coefficient under low pressure. The average rose from 0.60 to 17.52 kg/m²h$^{0.5}$. 

43
Table 1: Porosity, total water absorption, densities and capillary water absorption for the three directions of the tested samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>P (%)</th>
<th>W (%)</th>
<th>Densities</th>
<th>Capillary absorption: A (kg/m²h⁰⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\rho_0$</td>
<td>$\rho_s$</td>
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<tr>
<td>1</td>
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<td>2.09</td>
<td>2.43</td>
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<td>6.98</td>
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<td>2.39</td>
<td>2.59</td>
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<td>2.65</td>
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<td>9</td>
<td>10.53</td>
<td>2.98</td>
<td>2.36</td>
<td>2.64</td>
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<tr>
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<td>10.74</td>
<td>3.21</td>
<td>2.29</td>
<td>2.56</td>
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<tr>
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<td>2.18</td>
<td>2.60</td>
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<td>2.21</td>
<td>2.66</td>
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<td>10.14</td>
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<td>2.63</td>
</tr>
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<td>1.95</td>
<td>2.56</td>
</tr>
<tr>
<td>Max</td>
<td>25.94</td>
<td>10.14</td>
<td>2.43</td>
<td>2.68</td>
</tr>
<tr>
<td>Aver</td>
<td>15.03</td>
<td>5.13</td>
<td>2.23</td>
<td>2.63</td>
</tr>
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</table>
### Table 2: Karsten tube and Hardness test results for the three directions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Karsten tube Ck (kg/m²h⁰.⁵)</th>
<th>Hardness (HL)</th>
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<tr>
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<td>D1</td>
<td>D2</td>
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<tr>
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</tr>
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<td>1.99</td>
<td>1.78</td>
</tr>
<tr>
<td>6</td>
<td>1.02</td>
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</tr>
<tr>
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<td>0.80</td>
<td>0.43</td>
</tr>
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<td>1.95</td>
</tr>
<tr>
<td>9</td>
<td>1.90</td>
<td>2.56</td>
</tr>
<tr>
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<tr>
<td>Max</td>
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<td>17.85</td>
</tr>
<tr>
<td>Aver</td>
<td>4.95</td>
<td>4.91</td>
</tr>
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</table>
The average variation coefficient CV of the Karsten tube test was around 15 % for all directions, which is acceptable in terms of magnitude. Many factors such as reading errors and contact area could cause the variation in test results [11]. Concerning the superficial hardness, the average of the three directions varied from 285 to 526 HL with an average of 411 HL. The variation coefficient was about 16 % without exceeding 35% as a maximum value. This variability could be due to the heterogeneity of the calcarenite stones. For hardness measurements of 14 sites, Viles et al. [12] obtained variation coefficients of 15.57 % with the Piccolo, 18 % with the Equotip, 11 % with the Silver Schmidt and 5.20 % with the Classic Schmidt test. The anisotropy index values indicate a medium directional dependency with an average of 11 %.

3.2 Correlations
From Figure 2a it can be seen that the capillary water absorption coefficients obtained by the standard capillary rise method and Karsten tube test are linearly correlated for the three directions with good correlation coefficients (about 0.90). As the slopes of the three trendlines are approximately equal, a single linear correlation can be established for all directions, as shown in Figure 2b. From that relation, we can conclude that the water absorption (g/m²) is higher for the Karsten tube test than for the capillary water rise test. It is true that there is an additional pressure due to the water column but it is very low compared to the scale of capillary suction exerted by the pores of a stone [13]. It was confirmed, by visualization of the water adsorption with X-ray and neutron radiography, that the smaller the contact area, the higher the water absorption [11]. This was explained by the additional sidewards adsorption of the pores surrounding the contact area [6].

Furthermore, it is important to ascertain the anisotropy of natural stone since it determines its use for the carving of ornamental elements and its arrangement in a structure [14]. It could also control its durability. For example, in the archaeological site of Volubilis, some stones laid contrary to the stratum are affected by many deterioration patterns such as cracks, spalling and differential erosion because they are unable to withstand high compression [15]. It is therefore worthwhile identifying the sedimentary layering of the fresh replacement stones and of the blocks scattered on the ground of the site for future reassembly and restoration. Assuming that the lowest capillary water absorption values are measured perpendicular to the sedimentary layering [10; 16], the analysis of Tab. 1 and 2 shows that with the Karsten tube test, the layering of 80 % of samples can be determined (except samples 3,5,8,14,22).
Moreover, the Karsten tube test can be used to estimate the porosity and total water absorption of calcarenite stones. According to Figures 3a and 3b, the square root of the quantity of water absorbed between 2 min and 30 min is linearly correlated to the porosity and water absorption. It has been pointed out that the Karsten tube test is able to distinguish differences in open porosity: the higher the open porosity, the higher the water absorption measured by the Karsten tube [11].

Many researchers have proposed empirical equations to predict bulk density and porosity as a function of Schmidt hammer hardness. Linear correlations between both bulk density and porosity with Schmidt hammer hardness for granitic stones were established in [17]. The results of the study reported in [18], conducted on 19 rock types (10 igneous, 7 sedimentary
and 2 metamorphic), indicated that the porosity and Schmidt hammer hardness are linearly correlated. While there is no clear correlation between Schmidt hammer hardness and Piccolo Leeb hardness, the latter is closely linked to Equotip Leeb hardness [12].

Figure 4a reveals that the porosity and the hardness of the calcarenite stones are inversely proportional: the lower the hardness, the more porous the calcarenite. The variation in porosity as a function of Leeb hardness is linear with $R^2 = 0.95$. The bulk density of the calcarenite stones was estimated from the hardness using a linear equation with $R^2 = 0.96$ as shown in Figure 4b. Our results are comparable to the results of [19] performed on many rock types (sandstones, tuff, rhyolite, travertine, dolomite and granite) and the results of [20] conducted on 22 samples of different stones (sandstone, limestone, dolomite and marble), using Equotip Leeb hardness.

![Figure 4. Relationship between hardness and porosity with bulk density](image)

3.3 From laboratory to field
Many in-situ studies have used Karsten tube, Piccolo or Equotip hardness testers to characterize stone weathering [21; 22], to assess the effectiveness of treatments [19; 23], and to investigate the petrophysical properties of different building materials [24]. But to what extent can laboratory results be extrapolated to the field, i.e. in the present case Volubilis monuments or the Ain Schkor quarry? For the Karsten tube test, some researchers state that the moisture content in the stone influences the field performance of water absorption [23; 25], while others report that the variation in moisture content due to atmospheric conditions does not significantly influence the measurement compared to the standard deviation of the method itself [6]. Concerning the Piccolo Hardness test, [12] illustrated the insensitivity of the Piccolo and Equotip hardness testers to block size and edge effects unlike the Schmidt Hammer test [26]. The wetness of the tested surface could also influence the hardness measurement by the Piccolo device, but for the calcarenite stones in the archeological site of Volubilis and its quarry, the influence of in-situ relative humidity variations on hardness measurements is negligible. In fact, the calcarenite stone has a very low moisture adsorption. For instance, the maximum water content and saturation degree of calcarenite stone are
respectively \( w = 0.30 \% \) and \( S = 6 \% \) for \( H_r = 86 \% \), which is the annual average of maximal relative humidity in the region.

4. Conclusion

Physical properties of calcarenite stones such as the bulk density, porosity, total water absorption and capillary absorption were determined. Two non-destructive devices, the Karsten tube and Piccolo hardness tester, were used to measure the water absorption and Leeb hardness of the calcarenite stones. This study showed the possibility of estimating total water absorption, capillary absorption and porosity from the Karsten tube test. It also confirmed that the bulk density and porosity correlate well with the Leeb hardness. The two devices could then be used to study the calcarenite stones in Volubilis and its quarries. As perspectives of this study, we will investigate the correlations between Karsten water absorption and water permeability and between the Leeb hardness and mechanical strength.

References


[3] RILEM, T. C. 25-PEM Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods, Materials and Structures, 13(1980), 175-253


STRAIN CHANGES DURING THE PROGRESS OF WATER INFILTRATION IN TUFFEAU STONE

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Abstract
Calcareaous stones such as Tuffeau, which is used for the construction of French castles in the Loire valley, are highly affected by environmental conditions, in particular humidity and temperature changes and rain. The main degradation of this soft and porous limestone is a progressive spalling of thick plates (1 to 3 cm) from the surface of the stone. Our experimental program aims to assess the mechanism of spalling decay activated due to the coupling of mechanical, hydric and thermal stresses.
Concerning hydric action and in order to follow the behavior of the stone during water infiltration mainly near the surface, strain gauge rosettes were used. Four rosettes were placed on a sample of Tuffeau stone at different distances from the surface (1, 2, 4, 7 cm) to measure locally the strain during water infiltration. These rosettes determine the strain in three directions 0°/45°/90°.
In this communication, results concerning differential strains between the surface and the core of the stone due to water infiltration will be presented. They demonstrate the local contraction zone and expansion zone in each direction separately and show clearly the thicknesses of the surface which can be highly stressed due to the progress of water infiltration in the stone.

1. Introduction
Spalling is a surface degradation of building stones [1,2]. It can be described as the formation of a crack parallel to the surface of the stone exposed to the environment, generating a plate whose thickness is in the order of 1 cm. This plate eventually flakes off, leaving a powdered surface. The phenomena causing this degradation have not yet been established, although several hypotheses have been put forward and discussed [1-4]. However, there is a consensus concerning the role of water: this parameter can be the source of physical changes (e.g. changes
in mechanical properties, hydraulic dilation), and is a vector of degradation through the transport of pollutants, and the dissolution / crystallization of phases. In order to further our knowledge of the reaction of stone with respect to water migration, this communication presents the results of an experimental campaign applied to Tuffeau, which is a highly porous siliceous limestone. The experiment consisted in subjecting a stone sample to imbibition, and by monitoring strain at different heights in the sample.

2. Material and methods

2.1 Tuffeau
Tuffeau is the commonest building stone in the ‘Centre Val-de-Loire’ region of France. It was widely used for the construction of castles in the Loire Valley. This stone is affected by several forms of degradation including spalling and scaling. Tuffeau is composed of a major calcite phase (50%), a high siliceous fraction (40%; opal CT and quartz) and a significant clay content (10%; glauconites, smectites, illite). It is very porous (45 % of porosity), with a bi-modal (first peak at 8μm; the second at 0.01μm) porous network [5]. Table 1 summarizes the main mineralogical and physical properties of Tuffeau. The mechanical characteristics depend on the degree of water saturation and on the orientation with respect to the bedding plane [5-8]. The stone tested in this experimental campaign was extracted from the Usseau quarry, located in the Vienne department, in the Center-West of France.

Table 1: Mineralogical and physical properties of Tuffeau [2,5].

<table>
<thead>
<tr>
<th>Mineralogical composition</th>
<th>Calcite=50%, Opal CT= 30% Quartz=10%, Clay minerals=10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density</td>
<td>1.3 g/cm³ ±0.01</td>
</tr>
<tr>
<td>Skeletal density</td>
<td>2.5 g/cm³ ±0.01</td>
</tr>
<tr>
<td>Porosity</td>
<td>40 - 45%</td>
</tr>
<tr>
<td>Pore access diameter</td>
<td>5 μm</td>
</tr>
<tr>
<td>Permeability</td>
<td>10⁻¹³ m²</td>
</tr>
<tr>
<td>Compressive strength at dry state:</td>
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</tr>
<tr>
<td>orientation ⊥ &amp; // to bedding plane</td>
<td>11.67 MPa ± 0.33 &amp; 9.13 MPa ±0.35</td>
</tr>
<tr>
<td>Compressive strength at saturated state:</td>
<td></td>
</tr>
<tr>
<td>orientation ⊥ &amp; // to bedding plane</td>
<td>4.83 MPa ± 0.33&amp; 3.86 MPa ±0.15</td>
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<tr>
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<td>orientation ⊥ &amp; // to bedding plane</td>
<td>1.30 MPa ±0.11 &amp; 1.48 MPa ±0.09</td>
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<tr>
<td>Tensile strength at saturated state:</td>
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<tr>
<td>orientation ⊥ &amp; // to bedding plane</td>
<td>0.38MPa ±0.08 &amp; 0.51 MPa ±0.06</td>
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2.2 Sample preparation
The cylindrical Tuffeau sample, 40 mm in diameter and 80 mm in height, was cored in the
direction parallel to the bedding plane (i.e., the axis of cylinder is parallel to the bedding planes)
(Fig. 1). This direction was chosen because the imbibition procedure used can simulate actual
in situ imbibition due to rain on stonework. Four strain gage rosettes were glued on the lateral
surface of the cylindrical sample, at different heights: 10 mm (J1); 20mm (J2); 40mm (J3);
70mm (J4). Each strain gage rosette was composed of three strain gages, oriented at 0°, 45° and
90° depending on the eigenvectors of the loading, which correspond to the same directions as
the axes of symmetry of the sample. The rosettes are "KFG 120" type from Kyowa and were
glued using "CC-35A" glue. The diameter of each rosette was 1 cm. Before testing, the sample
was dried in an oven at 60°C during 92 hours. Then, it was cooled down in a desiccator with a
drying salt that maintains an almost zero relative humidity.

2.3 Methods
Before performing the imbibition test, cyclic mechanical loading tests were conducted to assess
the quality of gluing of the strain gages by controlling the repeatability of measurements.
Mechanical tests can also be used to control the orientation of the gages by analyzing the
orientation of strain with respect to the eigenvector of loading.

a. Mechanical test
The mechanical test was performed on a dry sample; it comprised cyclic loading between 0.5
and 1 MPa in compression. These stresses correspond to respectively 5% and 10% of the
compressive strength of Tuffeau at dry state and this ensures that the stress level is within the
limits of elastic behavior. The elastic behavior ranges up to 50% of the strength [9,10]. An
INSTRON 4485 press equipped with a 200 kN stress sensor was used for this test. Strain values
were acquired thanks to two NI 9235 modules with acquisition cards based on 120 Ω gages. A
macro program developed in LabVIEW 2013 software was used to give the mean value of 15
measurements every 5 seconds.
b. Imbibition test
The stone sample, in the dry state, was placed on a plastic grid that allows demineralized water to be imbibed into the sample by a capillary process. In addition to the three strain gage rosettes, a dial gage, with a standard deviation of $10^{-3}$ mm, was placed over the sample to measure the overall vertical displacement. An aluminum plate was placed between the upper face of the sample and the dial gage to avoid any measurement of singularity. During the test, the stone sample was subjected to imbibition. The test was completed when all the measurements (both strain gage rosettes and dial gage) had stabilized.

3. Results
3.1 Mechanical test results
Figure 2 shows the strain values measured by the strain gage rosettes during the cyclic mechanical loading. Dotted lines correspond to horizontal strain (H), the solid line to vertical strain (V) and the long dash line to tilted strain (T). Dotted lines were obtained by computing the mean value between vertical strain and horizontal strain. Negative strain corresponds to contraction while positive strain corresponds to extension.

![Figure 2. Strain values measured by the strain gage rosettes during the cyclic mechanical loading](image-url)
Along with cycles, results are repeatable. As expected, a contraction was observed in the vertical direction while extension occurred in the horizontal one, due to the Poisson effect [11]. Theoretically, since the loading was performed in the axis of symmetry of the sample, the eigenvectors of loading correspond to the vertical and horizontal axes as long as the material is homogeneous, isotropic, and within its elastic behavior. In this case, the tilted strain (T) should be equal to the mean of horizontal and vertical strain, which is represented by the blue line. This is correct for J1, J2 and J3, but is somewhat different for J4. For J4, a local material heterogeneity and/or a slight error of orientation may be the source of the discrepancy.

Thanks to the strain measurement, the Young’s modulus and the Poisson’s ratio can be calculated. These values are presented in table 2 and compared to literature data [12]. The comparison between the mechanical properties obtained by the cyclic mechanical test and literature data validate the strain acquisition protocol by rosettes.

Table 2: Comparison of mechanical characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (MPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\frac{\Delta \sigma}{\Delta \varepsilon_v})</td>
<td>(\frac{\Delta \varepsilon_h}{\Delta \varepsilon_v})</td>
</tr>
<tr>
<td>Strain gages</td>
<td>2128 ± 28</td>
<td>0.25 ± 0.007</td>
</tr>
<tr>
<td>Al-Omari, 2014</td>
<td>2037 ± 20</td>
<td>0.26 ± 0.005</td>
</tr>
</tbody>
</table>

### 3.2 Imbibition test

#### a. Dial gage results

Figure 3 shows the strain values calculated from the dial gage displacement during imbibition. These vertical strain values were deduced from vertical displacement based on the hypothesis of homogeneous strain. The solid line is the vertical strain value while the long dash line represents the height of imbibition.

![Figure 3. Vertical strain calculated from dial gage displacement during imbibition.](image)
At the end of imbibition, the resulting vertical strain reached $510 \, \mu\text{m/m}$, which is consistent with the characterization of Tuffeau in the literature [5,13,14]. A slight delay was observed between the end of global vertical strain variation and the end of visual imbibition: strain variation stabilized when the water front observed on the lateral surfaces was 5 mm below the upper surface of the sample. At that moment, the water front actually reached the upper surface, but only in the center of the sample.

b. Strain gage rosette results

![Figure 4](image-url)

Figure 4. Evolution of strain (H, V, T) during imbibition; height of imbibition

In order to describe the strain behavior of Tuffeau subjected to imbibition, 4 phases are proposed. Figure 5 is a zoom of figure 4 relative to strain gage #3 between 0 and 1.8 hours. This figure can be used to show the different characteristic phases of strain variation during imbibition.
Figure 5. Vertical strain (a) and horizontal strain (b) for strain gage #3 during imbibition, up to 1.8 hour.

The different phases are based on the variation in vertical strain. The first phase corresponds to a vertical contraction, while horizontal strain shows a slightly delayed beginning of extension. This phase begins with the start of imbibition and finishes when the height of imbibition is 5 mm below the lower border of the strain gage rosette. Strain gage rosette #2 and #4 follow the same trend: vertical contraction and delayed horizontal extension unless the imbibition reaches the strain gage rosette. For strain gage rosette #1, this phase cannot be seen since imbibition reached this gage almost immediately.

The second phase corresponds to both vertical and horizontal extension. During this phase, the amplitude of vertical extension is always higher than the horizontal one. This phase finishes when the water front is halfway up the strain gage rosettes (i.e. 5 mm below the upper border of the gage).

The third phase corresponds to a relative vertical contraction compared to the maximum value of extension reached during the second phase, while horizontal strain keeps on increasing, albeit more slowly.

Finally, the fourth phase corresponds to both vertical and horizontal extension, with limited amplitude. The final extension reached by vertical strain is similar to the local maximum value during the second phase. For the strain gage rosette #4, the behavior is singular since its fourth phase shows a higher amplitude of extension than the other gages.

4. Discussion

The 5 mm shift between visual lateral saturation of the sample and visual saturation of the core of the sample proves that the height of the water front at the core is greater than what can be seen on the lateral surface. We estimated that the difference was in the order of 5 mm during the whole imbibition. This particular profile is attributed to a border effect resulting from a local lack of capillary suction. The final value of the global vertical strain obtained by the dial gage is quite similar to the final value of local vertical strain measured by the strain gage rosettes. This proves that at the end of imbibition, the vertical strain is quite homogeneous in the whole sample. The variation of local values of vertical strain is not monotonous; it starts by contraction (phase 1), then extension (phase 2), then contraction (phase 3) and finally extension (phase 4), although the variation in global values of vertical strain is monotonous. This shows that during imbibition, the vertical strain is far from homogeneous. Concerning horizontal strain, its variation is more predictable:
there is no strain above the water front, and the strain of the imbibed stone increases progressively with time. Strain gage rosette #4 gave some singular values, which can be attributed to local material heterogeneity and/or a slight error of orientation, as concluded the mechanical test. Considering the phases of strain variation described in the results, the following hypothesis can be put forward to explain the behavior of stone with respect to water migration:

Phase 1 - During this phase, the water front has not yet reached the strain gage rosette. However, some strain effects can be observed: vertical contraction and a beginning of horizontal extension. The horizontal extension could be the repercussion of the horizontal extension of the part situated just under the strain gage, which is imbibed by water. However, because there is no water on the part relative to the strain gage location, this extension results from horizontal tensile stress. Due to the Poisson effect, horizontal tensile stress comes with vertical compressive stress, leading to vertical contraction, as observed on the strain gage rosettes. This effect is local, and the fact that the diameter of the strain gage rosettes is 1 cm may tend to underestimate this local effect if the height of the effect is smaller than 1 cm. The end of phase 1 corresponds to the presence of water in the core of the sample at the height of the lower part of the strain gage rosette.

Phase 2 – This phase corresponds to the expected effect of imbibition at the global scale, i.e. both vertical and horizontal extension due to water saturation. This phase ends when the water front in the core reaches the upper border of the strain gage.

Phase 3 – This phase begins when the water front is above the strain gage rosette. This vertical contraction could result from local water desaturation just after crossing the water front. This desaturation was observed by Beck [15] with a time lag between the visual saturation and the saturation in weight which ensure the total end of the imbibition. This local desaturation could be the non-linear consequence of the competition between two phenomena due to the bi-modal pore distribution of Tuffeau: capillary imbibition driven by capillary porosity (high speed, low suction) and saturation of smaller pores (low speed, high suction). Hence, once the water front driven by capillary absorption is passed, the available water must feed both phenomena (i.e. capillary imbibition of upper parts of the sample and progressive saturation of small pores) although it is provided by capillary imbibition only. This desaturation may not result in horizontal contraction because this local effect is vertically situated between two horizontal zones that are differently water saturated.

Phase 4 – Once the local effect of desaturation is completed, all the porosity progressively becomes saturated by capillary imbibition.

The main interesting feature of the results concerns the effect of imbibition on the local vertical strain, because it is not limited to monotonous extension. The existence of vertical contraction with significant amplitude (about $10^{-4}$ m/m during phase 1) is particularly relevant for identification of the degradation process at the origin of spalling. By comparison with in situ conditions of stones in a wall submitted to a rain event, the vertical contraction observed during the experiments corresponds to horizontal contraction perpendicular to the surface of the stone. If this contraction is restrained by boundary conditions such as a rigid joint or harder stone, it would result in tensile stress, situated just after the water front, i.e. around 1 to 2 cm depth. The amplitude of this tensile stress may not be neglected compared to tensile strength. This could be the origin of a crack parallel to the surface at 1 to 2 cm depth, which corresponds to the description of spalling.
5. Conclusion

This paper assessed the effect of water migration on the strain of a very porous limestone (Tuffeau) with a view to identifying the degradation process causing spalling. The strains were measured by using a dial gage and strain gage rosettes. In order to validate the experimental procedure based on strain gage rosette measurements, a cyclic mechanical test was performed. This preliminary test led to the conclusion that, for most of the strain gage rosettes used, the measurement was consistent with previous results and literature data.

The use of strain gage rosettes allows the identification of both vertical and horizontal strains during imbibition. Whereas horizontal strain follows a global tendency of monotonous and progressive extension during imbibition, vertical strain shows more diverse behavior, with alternating contraction and extension. We have put forward some hypotheses to try to explain the specific behavior of vertical strain.

The existence of vertical contraction at the height just above the water front can contribute to the debate about the origin of spalling. Indeed, this vertical contraction may correspond to horizontal contraction for in-situ stones in a wall exposed to rain. If the displacement of this stone in the direction of depth is restrained by a rigid mortar or a harder stone, it could result in significant tensile stress, able to generate a crack parallel to the surface. As the typical depth of water imbibition during a rain event in Tuffeau is between 1 and 2 cm, the depth of the crack would be around those values. Hence, this vertical contraction observed on a sample submitted to imbibition could be a key element in the explanation of the origin of spalling. Buckling experiments similar to that carried out by Wangler could be interesting to identify the role of clays in the tested stone [16].

References

COMPARATIVE STUDY OF PREHISTORIC, TRADITIONAL AND CONTEMPORARY ADOBE BRICKS FROM CYPRUS

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Abstract
Earthen architecture in Cyprus dates back to the Neolithic era. Up until the first half of the 20th century, adobe bricks were used extensively for the construction of load-bearing masonry walls. However, following the modernization of the local society, the urbanization trends and the introduction of industrialized building materials, the use of adobes declined. Contemporary adobes are produced by a limited number of local manufacturers using random raw materials and empirical techniques. As a result, the end-product is generally non-homogeneous with variable physico-mechanical properties.

This paper presents a comparative study between prehistoric, traditional and contemporary (19th - 21st century) adobes from Cyprus. Reported results include mineralogical and physico-chemical analyses of both raw materials and brick specimens sampled from prehistoric archaeological sites, 19th - 20th century traditional buildings and contemporary producers. The findings of the study show that traditional and contemporary adobes are to a great extent similar to the prehistoric bricks, taking into account their inherent inhomogeneity. Nevertheless, mixing of raw materials was probably the norm in prehistory; this practice has been gradually abolished in traditional and contemporary adobe production. It is anticipated that the current study will contribute towards improving the practices for local adobe production and will assist in the development of quality control methods for earthen materials, thus enhancing their use in contemporary sustainable construction.

1. Introduction
From antiquity until today, earth has proven to be an adaptable material which has accommodated a wide range of contexts and cultures in a variety of climates around the world [1]. There exist thousands of earthen monuments of built heritage internationally, which are a
testimony of the widespread use of earthen materials since ancient times. Archaeological findings and buildings in Mesopotamia, Turkistan, and Russia testify that adobe brick use existed from ca. 8000 to 6000 B.C. [2][3]. In the Mediterranean region, the Middle East, Syro-Palestine, and Anatolia, there is proof of the existence of earthen buildings and specifically of the use of adobe bricks from the Neolithic Era onwards [4][5].

Adobe masonry in Cyprus also dates back to the Neolithic era (8500 B.C– 4500 B.C) [4][6]; however, information from archaeological investigation reports on the production and use of adobes in Cyprus is rather scarce [6][7][8]. Adobes continued to be used on the island as the predominant building material up until the 19th – 20th century. During the past 100 years, though, big changes took place in the local building industry, which marginalized the use of adobes [9]. The modernization of the local society, the growing urbanization, the introduction of industrialized building materials and the adoption of national building codes and regulations imposed the implementation of engineering design [10] and resulted in the gradual loss of the empirical techniques and know-how regarding the production and use of adobes.

Today, in the framework of promoting healthy, environmentally-friendly and sustainable construction, the public and private sectors, the industry and the academia are showing a renewed and growing interest for the re-introduction of earthen materials in the construction scene worldwide [5][11]. Additionally, numerous protected earthen structures in historic and pre-historic settlements around the world require interventions which will secure their durability for future generations. Hence, there is an imminent need to re-discover and assess earthen architecture, either through restoration practices or contemporary environmentally-friendly construction. This need is also true for the case of Cyprus. The present paper presents a comparative study between prehistoric, traditional and contemporary adobes from Cyprus, aiming to identify similarities and differences in their production. The results are anticipated to contribute towards improving the practices for local adobe production.

2. Adobe Production in Cyprus

In prehistoric settlements, adobes were produced using soil from the immediate surroundings, [4]. Straw was the most typical fibre used, although other organic matter (e.g. leaves, plants and weeds) has also been found in various samples [4][12]; in coastal settlements, sea weed was often used.

Hand-moulding was the norm in neolithic adobe production, leading to end-products of irregular shape and size. The aforementioned practice was later (i.e. during the Bronze Age) replaced by casting adobes in uniform rectangular moulds, thus providing advantages such as fixed dimensions and faster/easier building [7]. Two methods seem to have been adopted for moulding adobes in the past [7]. The first method is similar to the one applied in vernacular adobe production, and starts by placing the mould on the ground and filling it with mud; this is followed by straightening the wet mix on the upper side, before removing the mud. This led to adobes of larger dimensions and straight parallel surfaces. According to the second method, the wet mixture was placed on the ground and a rectangular mould was pressed on
top to “cut out” the extra material [7]. This promoted faster production but produced adobes with a curved (plano-convex) upper surface [13].

Researchers have documented a great variety of sizes for prehistoric Cypriot adobes [12][14]; however, dimensions such as (l:w:h) 0.50 x 0.60 x 0.10 m were found repeatedly in a variety of settlements [4][8]. The use of a fixed unit of measurement for prehistoric Cypriot adobes is absent, most probably due to the fact that the human palm was used for measuring the end-products [7]. In some cases, adobes of different dimensions were used for the construction of more complex walls or walls of larger thickness in the same settlement. This proves that, according to the needs of each building, there was site- and use-specific production of adobes in prehistoric times.

During the 19th – 20th century, vernacular Cypriot architecture presents a wide use of adobe, especially in areas which lacked suitable and easily accessible natural stone (e.g. plains). The main building system for walls was adobe masonry laid on a stone foundation. Vernacular adobe production was similar to contemporary practices. The soil was indistinctively taken, either from the surface or from greater depths; it was then roughly processed for the removal of stones and organic matter and for the breaking up of clay lumps [6]. In a pit in the ground, the processed soil was mixed with water and fibre (most commonly straw, although reeds, seaweed and goat hair were also used [7]). The wet mix was allowed to “mature” for 3 days, before casting the adobes in moulds.

Double timber moulds, with open top and bottom, were used for the moulding process, which was similar to the first method used in prehistoric times. A greater “standardization” in the dimensions of the bricks, along with a reduction in their thickness, is noted in vernacular adobes, compared to the prehistoric ones. This probably aimed at faster drying and easier building, due to a reduced bulk density [7]. The most prevalent vernacular adobe dimensions were (l:w:h) 0.30 x 0.45 x 0.05-0.07 m. These dimensions are very similar to the ones which Vitruvius [15] had defined as standard (one foot per one and half feet per one palm: (l:w:h) 0.296 x 0.444 x 0.074 m) and are also identical to the dimensions found in contemporary adobe production. The production of adobes usually took place during the warm and dry summer months, when the weather conditions were considered favourable. Drying of the final product usually took around a week [6].

Contemporary Cypriot adobes are mainly produced by two manufacturers in the Lympia and Athienou areas (Figure 1). These producers generally follow the traditional production technology and empirical methods, albeit with some main differences. The clayey soil the Lympia producer uses, is brought from the area of Tseri (Figure 1). The Athienou manufacturer, on the other hand, uses soil from random excavations, which results in the production of batches with different properties. Mixing of soils is not a common practice, although the Athienou producer often randomly collects and mixes soils from building debris or excavations of various origins. Both contemporary producers define the adequacy of the raw material used according to their experience and the ‘good quality’ of the end product [9].

Large stones, organic matter and clay lumps, which are known to weaken the end-product [16], are not given due importance and are therefore not removed, revealing a general “ignorance” concerning existing international guidelines on soil selection and adobe
production. This impedes the homogeneity of the mix, creates weak points in the final product and generally affects negatively the physico-mechanical properties of adobes [17]. Both contemporary producers use mechanical means for the mixing of the raw material and allow the mixture to “mature” for 1-3 days before casting. Adobes are then moulded using aluminium double moulds, with dimensions (l:w:h) 0.45 x 0.30 x 0.05 m. The Athienou producer fills the moulds manually on ground covered by straw, while the Lympia producer uses shovels to fill the moulds directly on a concrete subsurface.

Contemporary adobes are to a great extent non-homogeneous and show variable physico-mechanical properties [18]. Hence, there is an imminent need to improve contemporary adobe production methods and in essence to enhance the properties and durability of the end-product. This will help promote the material on the market for use in contemporary sustainable construction.

3. Materials and Methodology

A number of adobe samples from a variety of locations, dating back to prehistory (PrA – nr. 7) (i.e. Neolithic settlements of Khirokitia and Kalavasos – Tenta and Bronze Age settlement of Marki – Alonia) and the 19th – 20th century (OA – nr. 6) (i.e. villages of Ag. Sozomenos, Dali, Lympia, Kition, Larnaca - Ancient Kition and Old Nicosia) have been collected. These were added to samples (CA – nr. 2) obtained from the two contemporary adobe producers in Lympia and Athienou. Figure 1 shows all sampling locations, while Figure 2 shows photo evidence of selected samples from the 3 time periods under investigation.

![Figure 1. Map of Cyprus showing sampling locations.](image-url)
Figure 2. Prehistoric (PrA), 19th – 20th century (OA) and contemporary (CA) adobe samples.

All samples were subjected to a series of tests aiming to provide information on the characteristics of the raw material used for their production. These tests involved mineralogical (XRD) and chemical (XRF) analyses, standardized wet/dry sieve analyses, Atterberg Limits and linear shrinkage tests.

4. Results and Discussion

4.1 XRF Chemical Analyses

Pellets prepared using 10-15 g of powder from the samples and 2% wax were analyzed semi-quantitatively using a Bruker S2 Ranger ED-XRF. The results are presented in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>SrO</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>Cl</th>
<th>SO₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrA</td>
<td>0.24ᵃ</td>
<td>4.45</td>
<td>54.41</td>
<td>1.33</td>
<td>0.38ᵇ</td>
<td>1.64ᶜ</td>
<td>18.43</td>
<td>3.38</td>
<td>2.57</td>
<td>0.89</td>
</tr>
<tr>
<td>OA</td>
<td>traces</td>
<td>9.91</td>
<td>38.78</td>
<td>1.76</td>
<td>0.37</td>
<td>0.19</td>
<td>34.98</td>
<td>6.77</td>
<td>4.70</td>
<td>1.02</td>
</tr>
<tr>
<td>CA</td>
<td>0.12</td>
<td>9.07</td>
<td>41.25</td>
<td>1.58</td>
<td>0.41</td>
<td>0.53</td>
<td>33.40</td>
<td>6.30</td>
<td>4.66</td>
<td>1.23</td>
</tr>
</tbody>
</table>

ᵃOnly the PrA samples from Khirokitia had an elevated average percentage of SrO (6.12%).
ᵇPresent only in the PrA Khirokitia samples.
ᶜOnly the PrA samples from Kalavasos – Tenta had an elevated average percentage of SO₃ (24.57%).

The dominant chemical elements found in all samples, irrespective of time period, were calcium, silicon, iron and aluminium. The presence of Al, Fe and Si is attributed to the high content of clay minerals in Cypriot soils [4], while the presence of Ca is either attributed to the high levels of calcite in the raw material [7][8], or to the purposeful addition of lime during the mix design. This is considered to improve the consistency/cohesion of soils and thus of adobes [19].

It is worth noting that OA and CA have higher Fe, Al and Si concentrations; this seems to be linked to higher clay contents in the raw materials used and hints towards a differentiation in the raw material selection for adobe production during the respective time periods.
SO₃ was found in high concentrations in the samples from the prehistoric Neolithic settlement of Kalavasos – Tenta. This chemical oxide, which implies the existence of gypsum, is also evident in the analysis of geological samples from the wider Kalavasos area [12], thus proving that local soils were used for the production of the adobes of the aforementioned settlement. Similarly, Sr, a chemical element of the mineral celestine (SrSO₃), may be rare around the island, but its presence in the area of Khirokitia is rather significant [4]; hence, the chemical analysis of adobe samples from the Khirokitia prehistoric Neolithic settlement showed relatively high levels of Sr.

4.2 XRD Mineralogical Analyses
Fine powder from all samples was examined using a Bruker D8 Advance XRD with continual rotation, a step of 0.01° and a scanning speed of 0.5°/min, within the angle range 2θ = 2°-65°. Typical scanning patterns (Figure 3) obtained were then analysed qualitatively using the ICDD PDF 2 database and semi-quantitatively using the Rietveld method [20].

![Figure 3. Typical XRD patterns of PrA adobes from the Neolithic settlements of Kalavasos – Tenta (left) and Khirokitia (right).](image)

Table 2: Average percentage (%) of minerals found in the samples tested.

<table>
<thead>
<tr>
<th></th>
<th>Gy</th>
<th>Cal</th>
<th>Qu</th>
<th>Cel</th>
<th>Alb</th>
<th>Cor/Chl/Ed</th>
<th>Kao</th>
<th>Ill</th>
<th>Mus</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrA</td>
<td>0.20b</td>
<td>55.84</td>
<td>6.53</td>
<td>1.04c</td>
<td>7.04</td>
<td>1.17</td>
<td>3.35</td>
<td>0.69d</td>
<td>1.37</td>
</tr>
<tr>
<td>OA</td>
<td>nd</td>
<td>42.02</td>
<td>10.45</td>
<td>0.63</td>
<td>26.62</td>
<td>10.05</td>
<td>5.31</td>
<td>2.97</td>
<td>2.08</td>
</tr>
<tr>
<td>CA</td>
<td>0.77</td>
<td>47.43</td>
<td>12.30</td>
<td>0.57</td>
<td>20.41</td>
<td>7.42</td>
<td>5.75</td>
<td>3.48</td>
<td>1.11</td>
</tr>
</tbody>
</table>

- Gy: Gypsum, Cal: Calcite, Qu: Quartz, Cel: Celestite, Alb: Albite, Cor/Chl/Ed: Corrensite/Chlorite/Edenite, Kao: Kaolinite, Ill: Illite, Mus: Muscovite.
- Only the PrA samples from Kalavasos – Tenta had an elevated Gy presence (43.01%).
- The PrA Khirokitia samples had a slightly elevated Cel average presence (1.47%). This was similar to the OA adobes from Kition and Ag. Sozomenos (average percentage 1.44%); OA from Dali and Lympia contained no Cel.
- Only one PrA adobe from Marki – Alonia had an elevated percentage of illite (18.74%).
The results of the mineralogical analyses are summarized in Table 2. These agree well with the XRF results and show that the dominant minerals in all samples were calcite, quartz and albite. The PrA Kalavasos – Tenta samples had high levels of gypsum; this is attributed to the use of gypsiferous soils from the wider Kalavasos area. The PrA Khirikiti samples presented a clear peak in the area of $2\theta=30.04^\circ$ (see Figure 3), which proves the existence of the mineral celestine.

OAs presented generally similar mineralogy, with high levels of calcite and no gypsum content, with the exception of the sample from the Old city of Nicosia, which had a very small percentage of gypsum, probably the result of secondary salt formation [21] due to atmospheric pollution in the urban environment of the capital city of Cyprus. Gypsum was also observed in the two CA samples tested.

It is worth noting that the XRD analyses confirmed the higher concentrations of clay minerals (i.e. corrensite, illite, albite, kaolinite and muscovite) in the OA and CA samples. This is linked to higher clay contents in the raw materials used and enhances the argument regarding the different selection of the raw material during these time periods, as opposed to prehistory.

### 4.3 Grain Size Distribution and Fibre Content Analysis

All samples were subjected to wet sieving in accordance with ASTM D422-63 [22]. During this test, the suspended fibres were manually collected to estimate their volume.

Table 3 presents the average percentage of fine grains (<75 μm) and fibre content (by volume) of the adobes under study. All samples had a very high percentage of fine grains; this agrees well with the results of the XRF and XRD analyses, which showed significant presence of clay minerals and related chemical elements respectively.

<table>
<thead>
<tr>
<th>Clay – Silt (&lt;75 μm)</th>
<th>Fibre Content (by volume)</th>
<th>Type of Fibre</th>
<th>Length of Fibre (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrA</td>
<td>57.57</td>
<td>traces</td>
<td>straw$^a$</td>
</tr>
<tr>
<td>OA</td>
<td>72.62</td>
<td>27.67</td>
<td>straw$^b$</td>
</tr>
<tr>
<td>CA</td>
<td>76.07</td>
<td>23.95</td>
<td>straw</td>
</tr>
</tbody>
</table>

$^a$Straw and other organic plant matter [14][24].
$^b$Traces of seaweed were found in the OA from the coastal area of Ancient Kition.

It is worth noting that international normative documents [23] suggest the use of raw material with clay/silt content between 5-70% for adobe production. Although these documents also state that adobe manufacturing is the least demanding earth building technique in terms of soil selection [23], it seems that a fair number of adobes produced in Cyprus in more recent years (i.e. OA and CA) is comprised of soil with excessively high (>70%) fine content. Prehistoric adobes, on the other hand, have lower percentages of fine grain contents, thus suggesting that prehistoric adobe producers were much more careful in the selection of their raw materials, or
at least familiar with the mixing of two or more different types of soil in order to achieve better properties of the end-product. This practice seems to have been lost through the ages. The high content of fines in Cypriot soils probably also explains why adobe masonry became the dominant earth building technique on the island. Monolithic wall masonry techniques, prevalent in neighbouring countries, needed much more sophisticated soil selection. Furthermore, due to the rich clay content of local soils, 19th – 21st century adobe producers have been mixing soils with large amounts of straw, typically more than 40 kg per m$^3$ of soil, to avoid shrinkage and cracking [6]. The results presented here (Table 3) indicate that OA and CA have an average fibre content of around 23% - 28% (by volume); this indeed corresponds to around 40 kg of straw per m$^3$ of soil.

PrAs investigated in this study presented no organic fibre. This is attributed to the decay of the fibre through the centuries. Excavation reports confirm the presence of straw (and in some cases of other organic plant matter) in all adobes examined in this research [14][24].

4.4 Atterberg Limits and Linear Shrinkage Tests

For determining the Atterberg Limits of the samples under investigation, all soils were sieved using the 0.425 mm (No. 40) sieve, and the material passing was tested according to BS 1377 [25]. The cone penetrometer was used for determining the Liquid Limit of the samples [25].

Although international normative documents generally do not indicate maximum linear shrinkage limits for soils destined for adobe production, a few of them [26][27] indicate restrictions regarding the number and size of cracks on the final product; these phenomena are directly correlated with the linear shrinkage of soils [23]. The linear shrinkage test was therefore also carried out on all samples according to the BS 1377 [25]. Table 4 summarizes the results of both the linear shrinkage and the Atterberg Limits tests.

<table>
<thead>
<tr>
<th></th>
<th>LL (%)</th>
<th>PI (%)</th>
<th>Linear Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrA</td>
<td>26.84 - 41.25</td>
<td>5.29 - 17.92</td>
<td>2.88 – 7.70</td>
</tr>
<tr>
<td>OA</td>
<td>30.47 - 39.64</td>
<td>9.35 - 15.66</td>
<td>5.87 – 12.43</td>
</tr>
<tr>
<td>CA</td>
<td>36.81 - 46.14</td>
<td>12.87 – 21.34</td>
<td>7.67 - 7.78</td>
</tr>
</tbody>
</table>

The Atterberg Limits and linear shrinkage test results also provide strong evidence of the clayey nature of Cypriot soils. It should be noted that, among all samples studied, only the two PrA samples from the Neolithic settlement of Khirokitia and the one CA sample from the Lympia producer, may be considered suitable for adobe production; the aforementioned samples fall in the Liquid Limit and Plasticity Index range suggested in the guidelines given by Houben and Guillaud [5]. It is interesting to note that Khirokitia is an area with soils with high percentages of calcite; this may have affected the Atterberg Limits results reported here. The results summarized in Table 4 additionally confirm the benefits of mixing soils for “correcting” the grain size distribution; this was most probably the norm in prehistoric times.
The linear shrinkage of the soils studied in this research is also very high, compared to values reported in the literature [23]. In most cases the results far exceed the maximum linear shrinkage allowed for building techniques such as rammed earth. This explains once again the lack of such techniques in Cypriot traditional earthen architecture and the prevalence of adobe construction on the island.

5. Conclusions

Although generally similar, the results of this study clearly demonstrate few but significant differences between prehistoric and 19th - 21st century adobes. The selection of soil from the immediate environment of the building site, the improvement of raw material by mixing two or more types of soil to achieve adequate grain size distribution and workability, and the variety of shapes, dimensions and uses of prehistoric adobes, prove that there existed a more advanced and complex understanding of the material in antiquity. Site- and use-specific adobe production offered sustainability, durability and longevity to the end-product, while the selection of soil from the immediate environment of the building also offered speed of construction. Most of this knowledge and practice seems to have faded through the centuries, while any surviving similarities with prehistoric production methodologies often occur randomly and by coincidence. This negatively affects the flexibility in use, the durability and the behaviour of more recent adobes. Hence, adobe today is treated as an inferior building material.

The results of this study clearly demonstrate the great importance and care which must be given to soil selection, investigation and mix design for the production of durable and thus truly sustainable earth building materials. In view of the increasing worldwide interest in earthen materials and techniques, in the framework of contemporary environmentally friendly building practices, additional research is needed on the effect of soil properties on the properties of adobes. The production of site- and use-specific adobes should be promoted, alongside the standardisation of soil selection and mixing procedure, in order to render the use of adobes viable in contemporary construction practices.

References


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LESSONS LEARNT FROM THE ANOMALOUS WATER SORPTIVITY OF STONES: THE CASE OF A CYPRIOT LIMESTONE

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(1) Department of Civil and Environmental Engineering, University of Cyprus, Cyprus

Abstract

One of the most common construction materials used all over the world is natural stone. In Cyprus, in particular, several monuments and historic buildings have been constructed using this material due to the diverse and accessible geological formations of the island. However, stone buildings, as well as cultural and architectural heritage stone structures, are affected by the presence of water, which mediates several decay mechanisms. This paper looks into the water sorptivity of a Cypriot limestone, which appears to deviate from normal expected behaviour. The anomalous water sorptivity of the stone under investigation suggests that the material possesses an inherent water repellency due to the presence of organic contaminants. This natural water repellency is exploited to develop a water repellent surface treatment. The efficiency and durability of the aforementioned treatment, as well as its effect on the pore system and the mineralogical composition of stone is investigated. The results strongly suggest that the water repellent treatment in question succeeds in permanently reducing the sorptivity of the Cypriot limestone and may therefore be used in conservation projects for the protection of stone facades.

1. Introduction

Natural stone is one of the oldest building materials. Up until the 20th century, the vast majority of buildings and structures worldwide were constructed with stone. Nowadays, the use of natural stone is limited. In Cyprus, in particular, despite the diverse and accessible geological formations of the island [1], stone is currently mostly used for decorative purposes and for the conservation of monuments of architectural and cultural significance.
The previous widespread use of natural stone was attributed to the fact that it was considered to be one of the most durable geomaterials. However, stone buildings, as well as cultural and architectural heritage stone structures, are affected by the presence of water, which mediates several decay mechanisms (frost action, salt crystallization etc.). Consequently, the protection of natural stone has drawn the attention of several scientists in the research community.

The use of hydrophobic and/or water repellent surface coatings for the protection of natural stone, in particular, has been discussed thoroughly [2]. Such coatings include acyl silicone products, water-based fluoralkylsiloxanes, polydimethyl siloxanes, phosphoric and polymaleic acid products [2-9]. The aforementioned polymers usually act by either blocking the stone pores or by restricting material breathability; in doing so, they affect the microstructure of the material and therefore enhance damaging mechanisms, such as salt crystallization.

Limestones have an unpredictable behaviour when water repellents are applied to them [10-11]. Furthermore, a limited number of studies [12-14] suggest that these stones have a natural resistance to water absorption, which may explain the aforementioned behaviour. This natural water resistance is indicated by an observed anomaly during water capillary absorption experiments, suggesting a reduced water wetting index ($\beta < 1$). Ioannou et al. [14], carried out capillary absorption experiments on a number of limestones using aqueous organic liquids (i.e. ethanol, 2-propanol, n-heptane) and water, before and after hydrogen peroxide and heat treatment of the samples; their results suggested that the low affinity of the limestone samples under investigation for water was a contact angle effect, possibly due to a layer of organic contaminants favouring partial wettability to water.

It is worth noting that, although calcite surfaces can be generally classified as naturally hydrophilic [15], many researches [12, 14, 16, 17] state that carbonate minerals exposed to the natural environment have the tendency to acquire organic adlayers which may potentially affect them. The most severe modification of calcite surfaces is attributed to the absorption of carboxylic and especially fatty acids. Since such an adsorption increases strongly and regularly with increasing homolog chain length [18], short chain fatty acids (C$_4$ to C$_{12}$) are not permanently adsorbed on calcite surfaces. Instead, the long, straight chains of fatty acids with more than 12 carbon atoms and the small size of the carboxyl groups allow them to form a nearly close-packed hydrocarbon layer above the calcite surface, which excludes water and prevents desorption and carbonate dissolution [12]. The aforementioned layer is formed due to the alkyl units of the long straight chains of the fatty acids, which are considered to be hydrophobic [12, 14, 18].

In this paper, we present new results confirming the anomalous water absorption of a Cypriot limestone. A surface treatment, based on the inherent composition of the sample under study, using oleic acid, is further tested. The efficiency and durability of this treatment, as well as its effect on the pore system and the mineralogical composition of the stone in question is thoroughly investigated. The results strongly suggest that the oleic acid water repellent treatment succeeds in
permanently reducing the sorptivity of the Cypriot limestone and may therefore be used in conservation projects for the protection of relevant stone facades.

2. Experimental Work

A Cypriot limestone originating from the area of Agios Theodoros, which belongs to the Pachna Formation [1], was used in this study. This stone is a light grey (according to Munsel Soil-Color charts) packstone or poorly washed biotsparite. Its intergrain cementing material is microsparry calcite with a small portion of micrite [1]. The stone under investigation has a complex mineralogy. Even though it is dominated by the presence of calcite, as expected, it also includes significant amounts of clay minerals (e.g. chlorite, montmorillonite), quartz, aragonite, potassium feldspar (orthoclase, microcline), zeolites (analcime), pyroxenes (augite) and plagioclases (anorthite, albite). Table 1 summarizes the mineralogical composition of Agios Theodoros stone.

Table 1: General details and mineralogical composition of the Agios Theodoros sample under study.

<table>
<thead>
<tr>
<th>Petrological family</th>
<th>Dimensions (mm)</th>
<th>Colour (Munsell Chart)</th>
<th>Mineralogy (XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agios Theodoros</td>
<td>70 x 70 x 70</td>
<td>5Y 7/2 Light Grey</td>
<td>calcite (67%), quartz (6%), clinopyroxene (5%), chlorite (4%), plagioclase (6%), K-feldspar (1%), aragonite (11%), montmorillonite and analcime (traces)</td>
</tr>
</tbody>
</table>

Capillary absorption experiments, in accordance with EN 1925 [19], were undertaken to determine the sorptivity ($S$) of the Agios Theodoros stone sample under investigation to water and a range of organic liquids (i.e. ethanol, 2-propanol, n-heptane). The results were plotted against ($\frac{\eta}{\sigma}$)$^{1/2}$, where $\sigma$ [$Nm^{-1}$] is the surface tension and $\eta$ [Ns$m^{-2}$] the viscosity of the wetting liquid at each temperature. According to Taylor et al. [13], the intrinsic sorptivity ($S_i$) and the water wetting index ($\beta$) of a sample can be calculated from the graphs using the following equation:

$$ S = S_i \left( \beta \ast \frac{\sigma}{\eta} \right)^{1/2} $$  \hspace{1cm} (1)

Oleic acid, purchased from Aldrich Chemical Co., was used in order to control the wettability of the stone under study. The latter is a fatty acid, which contains 18 carbon atoms; when used as an
organic additive [20], it has the ability not only to control the nucleation and growth of CaCO₃, but to also modify its surface [21]. In the research carried out by Walker et al. [6], the use of oleic acid induced additional hydrophobicity to the calcite surface of the York Minister Cathedral; this led to its protection against sulfation. In the present study, a solution of oleic acid (concentration 0.5\% w/w) was applied to the stone sample under investigation by brushing its top surface. Following brushing, the sample was allowed to dry at room temperature. In order to observe the effect of the treatment, the sorptivity of the treated sample was determined through capillary absorption experiments using water and organic liquids at different temperatures.

The durability of the oleic acid surface treatment was investigated by subjecting the test specimen to wetting-drying cycles using vacuum saturation. Drying took place in an oven at 105\°C, until constant weight was reached. Ten cycles of wetting-drying were performed. After each cycle, the sorptivity of the sample was determined through water capillary absorption tests.

The mineralogical composition of the specimen after the treatment was also determined through X-Ray Diffraction Analysis using a Bruker D8 Advance XRD instrument. The sample was first finely pulverized before being analyzed in the range 2\( \theta \) = 2-100\° with scan speed 2\(^{\circ}\)/min. The ICDD PDF 2 database was used for the qualitative identification of minerals.

The effect of the oleic acid surface treatment on the pore system of the specimen was investigated through Mercury Intrusion Porosimetry (MIP). A porosimeter supplied by Micrometricis was used for the MIP tests. The sample was subjected to a maximum pressure of 4.14 x 10\(^5\) kPa, assuming a mercury contact angle of 130\° and a surface tension of 4.85 x 10\(^10\) Nmm\(^{-1}\). In order to avoid including surface imperfections in the porosity estimation due to the irregular shape of the sample, a filling pressure of 10.3 kPa (1.5 psi) was adopted [1].

3. Results and Discussion

3.1 Capillary Absorption Measurements
Since the cumulative capillary absorption \( i \) increased linearly with the square root of time \( t^{1/2} \) for the sample under study, the sorptivity \( S (=i/t^{1/2}) \) was derived from the slopes of the respective graphs. As seen in Figure 1, when the sorptivity values were plotted against \( (\sigma/\eta)^{1/2} \), the data points fell into two distinct separate straight lines, which increased linearly. The water data line had a significantly lower slope. This is in line with previous related work [13-14], which showed similar anomalies during water capillary absorption in the case of limestone specimens.
Fox and Zisman [22] and Taylor et al. [13] state that pure organic liquids, like the ones used in this study, have low energy tensions and, therefore, exhibit complete wetting with wetting index ($\beta$) equals one. When water is used as the acting liquid, however, partial rather than complete wetting of the limestones seems to exist; the slope of the respective line in Figure 1 implies a wetting index $\beta=0.26$ (see Table 2). This can be explained by a degree of hydrophobicity of the calcite surface of limestones, which seems not to have a good affinity for water. Taylor et al. [13] and Ioannou et al. [14] suggest that the anomalously low water sorptivities of limestones are probably the result of organic contamination, due to the presence of a low-energy adlayer on the specimen’s surface.

Table 2: Water Wetting Indices before and after all treatments for the Agios Theodoros sample under study.

<table>
<thead>
<tr>
<th>Intrinsic Sorptivity ($\times10^{-4}$ mm$^3$)</th>
<th>Water Wetting Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
</tr>
<tr>
<td>Agios Theodoros</td>
<td>4.83</td>
</tr>
</tbody>
</table>

Figure 1. Sorptivity values $S$ versus $(\sigma/\eta)^{1/2}$ for the Agios Theodoros limestone.
3.2 Treatment with oleic acid (0.5 w/w)
Figure 2 shows the results after the oleic acid surface treatment. These indicate once again a linear behavior between the sorptivity $S$ and $(\eta/\bar{s})^{1/2}$. The organic liquids line remains generally unchanged after treatment with oleic acid (0.5% w/w), whereas the water line has an even lower slope.

![Figure 2. Sorptivity values $S$ versus $(\eta/\bar{s})^{1/2}$ before and after treatment with oleic acid (0.5% w/w) for the Agios Theodoros limestone.](image)

In Table 2, the actual reduction (ca. 98%) in the water wetting index of the sample after the oleic acid treatment can clearly be seen. This, strongly indicates that oleic acid adsorbs well on the calcite surface of the sample and induces to it additional hydrophobicity. The latter is attributed to the deposition of the resulting Ca(C$_{17}$H$_{33}$COO)$_2$ onto the calcite (CaCO$_3$) surface of the Agios Theodoros sample under investigation. The chemical reaction can be described according to Eq. 2.

$$\text{CaCO}_3 + \text{C}_1\text{H}_3\text{COOH} \rightarrow \text{Ca(C}_1\text{H}_3\text{COO)}_2 + \text{HCO}_3^-$$

3.3 Wetting/Drying Cycles
The results of the sorptivity tests after wetting and drying are shown in Figure 3. The sample is still very much partially wetted after 10 cycles of wetting and drying ($\beta = 0.03$) (see Table 2). Tests with pure organic liquids were also performed after the wetting-drying procedure; the organic liquids line, and consequently the intrinsic sorptivity of the sample, remain unchanged.

Although there is an increase in the water wetting index of the sample after wetting and drying, the latter retains its hydrophobicity. In fact, there is an 88% reduction in the original water wetting
index of the stone, even after the 10 cycles of wetting/drying. This result once again confirms that oleic acid adsors well on calcite surfaces.

Figure 3. Sorptivity values $S$ versus $(\sigma/\eta)^{1/2}$ for the Agios Theodoros limestone before and after treatment with oleic acid (0.5% w/w) and after 10 cycles of wetting-drying.

Figure 4. XRD patterns for the sample under study. Black line: Treated surface. Grey line: Untreated surface. C-Calcite, Cl-Chlorite, Q-Quartz, M-Montmorillonite, Al-Albite, Ar-Aragonite, Ac-Analcime, Au-Augite, O-Orthoclase, An-Anorthite.
3.4 X-Ray Diffraction Analyses
X-Ray Diffraction Analyses (see Figure 4) were performed on powder samples originating from 2 different areas of the test specimen (i.e. treated and untreated surface). From these, one may conclude that the mineralogical composition throughout the bulk of the sample under study has remained unaltered after the oleic acid treatment. The results show that the specimen still contains significant amounts of clay minerals (i.e. chlorite, montmorillonite). In fact, the relatively low original water wetting index of the stone may be attributed to the high amounts of clay minerals it contains; these are known to contain significant amounts of organic impurities, such as fatty acids [23].

3.5 Mercury Intrusion Porosimetry
The MIP results for the sample under study are shown in Figure 5. It is worth noting that MIP tests were performed on samples originating from the same areas as the samples subjected to X-Ray Diffraction analyses (i.e. treated and untreated surface).

![Figure 5. Pore size distributions determined using Mercury Intrusion Porosimetry (MIP).](image)

The results clearly indicate that the oleic acid treatment did not affect the pore system of the sample under study, since there is no difference in the pore size distribution between the two areas analyzed.

4. Conclusions
This paper confirms the inherent water repellency of the Agios Theodoros limestone. The latter shows anomalously low water sorptivity when subjected to capillary absorption experiments with
water and organic liquids at different temperatures. This anomaly is attributed, according to previous research work, to the presence of a hydrophobic organic contaminants adlayer below the specimen’s surface. The latter is possible, bearing in mind the significant presence of clay minerals in the stone under investigation.

The natural water repellency of the Agios Theodoros limestone has been exploited to develop a water repellent surface treatment based on the use of oleic acid. Capillary absorption measurements through the treated surface of the sample under study strongly suggest that the oleic acid treatment succeeds in reducing further the water absorption of the Agios Theodoros limestone. The efficiency of the aforementioned treatment was further investigated through wetting and drying cycles. Data from capillary absorption measurements after these cycles reveal that the oleic acid adsorbs well on the calcite bearing surface of the limestone tested. X-Ray Diffraction analyses and Mercury Intrusion Porosimetry tests indicate that the treatment does not affect the mineralogical composition or the pore system of the sample.

This work has practical significance since the results strongly suggest that the water repellent oleic acid treatment developed may be used to permanently reduce the sorptivity of the Agios Theodoros limestone; therefore, the aforementioned treatment may be used in conservation projects for the protection of monumental and other stone facades.

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FLUID MORTARS FOR FILLING LARGE CRACKS

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Abstract
The design and application of repair mortars based on traditional materials and following the requirements of compatibility in order to preserve historic masonry is very common in the last decades. Bedding mortars, renders/plasters and grouts have been used taking into account the specific needs of the masonry as well as the neighbouring materials and the environment in which the repair mortars will function. In some cases the existence of large cracks (of wide opening and significant length) in masonry is inevitable. Filling such discontinuities requires special design mortars in order to maintain prolonged fluidity, adequate cohesiveness and penetrability. At the same time, these mortars have to present volume stability, durability and compatible physical and mechanical properties with the neighbouring materials. In this paper a case study of fluid mortar designed for filling large cracks is discussed.

1. Introduction

Masonry structures constitute a countless number of different types of constructions dated from prehistory to present in which many values such as historic, archaeological, aesthetic, symbolic, social, cultural and scientific/technological are included making them a real treasury of human civilization [1]. According to Burman, the survival of masonry structures is essential to the spiritual, emotional and economic well-being of humans [2]. Preserving the masonry has different aspects: conservation/consolidation from decay phenomena due to the ageing effects of the environment impact on the buildings but also prevention of collapse mostly attributed to the inherent inadequacy of historical masonry structural systems to bear horizontal loads. Any intervention in order to anticipate these problems requires respect to the “values” of monumental character structures, including architectural integrity, authenticity of the materials and morphology. What is recommended in conservation is to use compatible to
authentic materials and traditional skills for their appliance. The most important characteristics or criteria by which compatibility is driven are:

- surface features (color, texture, roughness)
- composition (type of binder, granulometry of aggregate)
- strength level (compressive, tensile)
- elasticity (modulus of elasticity, deformability)
- porosity (porosity, pore size distribution, capillarity)
- coefficient of thermal dilation

These criteria have been applied in designing the repair mortars of a great number of interventions in Greece from the 90s up to nowadays and proved very successful and long lasting [3] [4].

Two different approaches in relation to interventions prevail: reversible and irreversible ones. Irreversible interventions aim at consolidating the mass of the masonry in particular when it suffers from softening due to intensive deterioration. The most common irreversible interventions are:

- grout injection
- deep repointing
- reconstruction of masonry missing parts
- punching steel bars (stainless steel) to saw cracks.

In irreversible interventions a major compromise between principles of restoration and safety and durability issues for the constructions is continuously under question. Grouts and mortars are inserted into the masonry mass by different techniques to fill cracks, voids in brick-mortar interfaces and reduce the intrinsic heterogeneity and anisotropy of the masonry. In most cases a tailored to the specific monumental structure grout/ mortar mixture is proposed taking into account the characteristics and pathology of the structure. Ready mixed grouts or mortars are not usually used since they do not often comply with specific requirements imposed by compatibility. From the 70’s and afterwards, grout injections have been used in many historical buildings and monumental structures. The grouts are slurries of a hydraulic nature binding system with or without inert fines and admixtures. The water/binder ratio is usually around 1.0. To be efficient, grouts must present in fresh state adequate fluidity and consistency, penetrability and volume stability. In addition, after hardening they must develop good bonding within the old masonry microstructure and mechanical strength. They usually fill small cracks [5]. To keep compatibility principles in designing grouts for historical masonry implies the selection of inorganic and relatively low strength potential binders, such as lime-based binding systems, which are the constituents of most of the joint mortars of ancient masonries. In literature, there are recommendations [6] [7] about the selection of raw materials, methods of testing grout performance and checking the filling effect after hardening.

In the case of cracks of large opening (2-10 cm) and significant length (often running the whole masonry) the application of grouts is not possible for both functional and aesthetic
reasons. On the other hand, a typical mortar cannot be applied as penetrability is difficult to be achieved. In such cases it is preferable to use a specially designed mortar which presents fluidity and contains aggregates in order to confer to volume stability and reduce shrinkage cracking. A mortar with special fluidity which under the force of gravity (or by low pressure) can cover the gap and add continuity to the masonry should also fulfil some requirements.

In the fresh state, it should present sufficient fluidity even 1 hour after preparation to assure penetrability under gravity and sufficient consistency. The particle size of the aggregates should be proper in relation to the crack width. The sand gradation is based on the crack width and a relation of \( d/D \geq 3 \) is used, where \( d \) is the smallest diameter of the crack and \( D \) is the maximum grain diameter [7]. During setting, the fluid mortar should be characterized by stability in order to avoid segregation, compatibility without any side effects (for example to avoid chemical reactions with stones), reduced shrinkage and good setting after injection and within the masonry.

Finally, in the hardened state, the required properties are compatibility with existing structure in terms of strength, porosity, thermal expansion coefficient, low water-soluble salt content and adhesion in order to present similar behaviour to deterioration agents with the whole masonry.

2. Case study- Galerious Complex

The Galerious Complex is located in the heart of Thessaloniki. It was built around 300 AD on a straight axis ranging from the North to the South including buildings like the Rotonda, the Triumphant Arch (Kamara), the Palace, the Octagon and the Hippodrome. The dominant masonry type at the Galerious Complex is theopus mixtum which is characteristic in late Roman period buildings. The walls are constructed with successive zones of rough stones and bricks with a strong mortar (2-5 MPa compressive strength) as binding material. The masonry structure and alignment present several defects which are covered by a thick-layer plaster coating. The stones used, came from the local green stone quarries located near the old Roman city [8].

The buildings' masonry, brick or alternating courses of stone and brick, had suffered major damage. The most serious problem was on the brickwork masonry’s faces, where there was extensive erosion of vulnerable materials, bricks and mortar. Settlements, earthquakes and abandonment were only some of the causes that led to masonry cracking. Further problems were created by uncontrolled natural growth on the site. In some places the masonry has shifted and open cracks have been formed (Fig.1). Additional problems were created by inaccurate interventions during the 1970s, done on a limited scale to consolidate the walls with cement mortar. The restoration project of the Palace started in 1994 and one of the main tasks was to conserve the old masonries.
The static analysis of the masonry has shown that there was no need for reinforcement. The people responsible for the monument decided to fill the cracks in order to restore the continuity of the structure. In this frame, a fluid mortar was decided and technical guides were given to technicians to fill the cracks from bottom and proceed onwards, based on the grouting technique. This could be applied after sealing the crack using formwork blocks.

The composition of the mortar was based on the analysis of the original structural mortars, taken from the old masonries. To decide upon the proportioning of the mortars a few trial compositions were prepared. The composition that satisfied the criteria of compatibility with the characteristics of old mortar was based on lime and pozzolana and presented 7.0 MPa strength at the age of 3 months and 16-17% porosity (composition1). The data from the analysis of the old mortar are given in Table 1.

Table 1: Characteristics of old mortars

<table>
<thead>
<tr>
<th>Type</th>
<th>Binder type</th>
<th>Aggregate Type</th>
<th>Max size</th>
<th>Comp. strength MPa</th>
<th>Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old mortar</td>
<td>L+P</td>
<td>Natural sand</td>
<td>8mm sand</td>
<td>3.5-4.0</td>
<td>16.7-18.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+crushed brick</td>
<td>4mm bricks</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

L=lime P= pozzolan
3. Results

In relation to the repair mortar designed for filling large cracks, the binder was lime and natural pozzolan. A small proportion of clay was also tested in a trial mixture for colour adjustments. This mixed binder type presents adequate strength, compatibility, durability to ageing and reduced cracking tendency [9] [10]. As the widths of the cracks present variations, with the smaller opening being equal to 1cm, the aggregates selected were natural sand of size 0-8 mm. Crushed brick of specific granulometry was used according to the analysis of the masonry mortar. In order to achieve the required workability without causing strength reduction, carboxylic basis superplastisizer (chemium 174 produced by Domylco) was added in high proportion. Additionally, a viscosity modifier (VMA) was used as additive. In this way, the setting was retarded and the mixture remained workable for longer. Table 2 indicates the proportion of the trial mixtures.

<table>
<thead>
<tr>
<th>Lime</th>
<th>Pozzolan</th>
<th>Fine clay</th>
<th>Sand 0-8mm</th>
<th>Crushed brick 2-4mm</th>
<th>Limestone filler</th>
<th>W/B</th>
<th>Superplas. % of binders</th>
<th>VMA % of binders</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.2</td>
<td>2.4</td>
<td>0.4</td>
<td>0.7</td>
<td>0.61</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.9</td>
<td>-</td>
<td>2.4</td>
<td>0.4</td>
<td>0.8</td>
<td>0.64</td>
<td>3.0</td>
</tr>
</tbody>
</table>

As workability is a crucial parameter, it was tested both by flow table (EN1015-3:1999 without any vibration beating) and by L-box as seen in Figure 2. The L-box test is used to evaluate the fluidity of self-compacting concrete and its ability to pass through steel bars. The L-box consists of a vertical section and a horizontal section. With the L-box, the height of concrete in the vertical section, h, the height of concrete in the horizontal section, h2, and the time for self-compacting concrete to reach 40 mm from three steel bars, T, can be measured. When the ratio of h2 to h is larger than 0.8, self-compacting concrete has good passing ability [11]. Based on the above principle, both compositions presented good fluidity.

Figure 2. Testing the workability of fresh mixtures
At the age of 28 days mechanical and physical properties were tested. The results are shown in Table 3. Also, the volume change of the compositions was recorded in time (Fig. 3). The volume change was higher for composition 2.

Table 3: Mechanical and physical properties of the repair mortars

<table>
<thead>
<tr>
<th>Spec gravity</th>
<th>Porosity %</th>
<th>Compr. Strength MPa</th>
<th>Flex. Strength MPa</th>
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<tbody>
<tr>
<td>1</td>
<td>1.83</td>
<td>20.8</td>
<td>6.50 2.65</td>
</tr>
<tr>
<td>2</td>
<td>1.93</td>
<td>21.5</td>
<td>14.28 2.90</td>
</tr>
</tbody>
</table>

Figure 3. Volume change of the trial mixtures for composition 1 (left) and for composition 2 (right)

The results showed that both compositions present acceptable (based on the criteria set) properties. Composition 1 based on lime and natural pozzolan was selected as the compressive strength of 6.5 MPa was satisfactory according to the analysis of the old mortars; the stability of this composition was acceptable. Also, the properties of composition 1 at the fresh state were preferable. Having fulfilled the criteria for a fluid and effective mortar, composition 1 was proposed to be produced on site.

4. Conclusions

The formation of large cracks in historical masonries is a common problem. Earthquakes or settlements are the main reasons for causing such large discontinuities. When preservation, in order to restore the continuity, is the question, specially designed mortars that combine fluidity, penetrability, good adhesion, compatibility, durability and at the same aesthetic harmonization with the rest of the masonry, is required. The design has to start from the binder selection and the type and size of the aggregates. Fine materials and additives are also necessary in order to obtain fluidity. Criteria of compatibility with the neighbouring materials of the masonry can be overcome if the design is based on the results from the analysis of the old materials. Applying this fluid mortar also requires some experience and is essential for a successful intervention.
References


CATALYTIC EFFECT OF CARBONIC ANHYDRASE ENZYME ON LIME MORTAR CARBONATION

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Abstract
Carbonation reaction of lime in the presence of carbonic anhydrase (CA) enzyme from bovine erythrocytes has been studied to explore its effects on the reaction kinetics, precipitation and phase transformations of calcium carbonate and strength development of mortars. Results clearly indicate an enhancement of calcium carbonate precipitation and a significant modification of calcite crystal morphology in the presence of the enzyme. CA accelerated the phase transformations from amorphous calcium carbonate (ACC) into calcite via an intermediate phase formation of anhydrous ACC and vaterite. When compared to the pure solution in which ACC formed and subsequently transformed to rhombohedral calcite, in the presence of CA enzyme calcite was formed with a morphology that was substantially modified from the equilibrium rhombohedral form with the appearance of new crystal faces. In lime mortar higher degree of CaCO₃ precipitation, and faster and higher strength development was recorded in the presence of enzyme. Inspired from nature, the kinetic effect that CA enzyme has on lime carbonation might offer a potentially novel approach with significant benefits on the applications of lime mortars in architectural heritage conservation.

1. Introduction
Carbonation is the essential process in the setting and hardening of traditional masonry lime mortars. When fresh lime mortar mixture is exposed to atmospheric conditions, it hardens by a chemical process of carbonation as a result of the reaction between CO₂ in the atmosphere and calcium hydroxide (Ca(OH)₂) in the pore solution following the overall reaction as follows:

\[
\text{Ca(OH)}_2(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{CaCO}_3(s) + 2\text{H}_2\text{O}(l)
\]  (1)
This reaction is principally controlled by two main mechanisms: (i) diffusion of the atmospheric CO$_2$ gas through the porous system up to the reaction front, and (ii) reaction between the dissolved CO$_2$ and Ca(OH)$_2$. Diffusion phenomenon is slow relative to the chemical reaction because water saturation degree in the porous space influences CO$_2$ diffusion rate [1,2]. Water, which is present in the initial state of the mortar and is released during the reaction, will hinder the CO$_2$ diffusion the rate of which will depend on the pore system, drying rate, capillary transport regime and capillary condensation.

Due to the low liquid-to-solid ratio ($< 1$) carbonation process in lime mortars follows a complicated process which is different from industrial carbonation performed as a liquid-film or suspension process by bubbling CO$_2$ through a suspension (liquid-to-solid ratio $> 5$) for which more models exist. The reaction proceeds stepwise from the surface into the core of the mortar due to the CO$_2$-diffusion process. The carbonation of lime takes place within the alkaline pore water ($\text{pH} \approx 12.5$) of the mortar where the loosely hydrated aqueous form of dissolved CO$_2$ (reaction 2) hydrates with OH$^-$ ions, and dissociates into bicarbonate (HCO$_3^-$) (reaction 3) and carbonate (CO$_3^{2-}$) (reaction 4) ions which eventually combine with Ca$^{2+}$ ions to form CaCO$_3$ through nucleation and subsequent crystal growth (reaction 5). Under such alkaline conditions HCO$_3^-$ ions can be formed directly and rapidly, but the rate of reaction 3 is slower than that of reaction 4, while reaction 5 is known to be instantaneous [3]. Therefore, reaction 3 is the rate-controlling step in the overall chemical reaction of carbonation in lime mortars.

\[
\begin{align*}
\text{CO}_2(g) & \leftrightarrow \text{CO}_2(aq) \\
\text{CO}_2(aq) + \text{OH}^-(aq) & \leftrightarrow \text{HCO}_3^-(aq) \\
\text{HCO}_3^-(aq) + \text{OH}^-(aq) & \leftrightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \\
\text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) & \leftrightarrow \text{CaCO}_3(s)
\end{align*}
\]

Due to the diffusion-related factors and low CO$_2$ concentration in the atmosphere, carbonation reaction of lime mortar proceeds gradually. The chemical reaction of carbonation starts only after the setting period involving plastic shrinkage and subsequently an initial strength gain occurs upon drying. Once open space is formed as a result of drying, the carbonation reaction is allowed to take place with the diffusion of CO$_2$ through this open pore space and its dissolution in the capillary water in liquid phase [1,2]. Slow kinetics of carbonation reaction in lime mortars implies slow kinetics of setting and hardening which significantly hinders their application in restoration practices. Additives such as polysaccharides, proteins, fatty acids and plant extracts such as Nopal juice are known to have been traditionally used to improve lime mortar properties [4]. However, they have a negligible impact on the carbonation reaction kinetics. Some organic compounds such as alcohols, citric acid, sucrose, calcium lignosulfonate and carbamates have been studied as additives to increase the carbonation reaction rates but the results are generally poor [5,6]. This is because such additives do not change the kinetics of conversion of hydrated CO$_2$ into HCO$_3^-$ ions, which is the rate-controlling step of carbonation reaction in lime mortars.
Bioinspired approaches from nature can provide a novel solution to master the kinetics of carbonation reaction in lime mortars. Carbonic anhydrase enzyme (CA) is a particularly efficient biocatalyst that takes part in many processes in living organisms such as respiration, CO₂ transport and photosynthesis, promoting the hydration of CO₂ and the production of HCO₃⁻ ions [7]. This enzyme plays an important role in microbially-induced calcium carbonate precipitation process. This has inspired many researchers to develop novel biomimetic strategies using CA enzyme as a catalyst CO₂ sequestration in industrial applications. CA enzyme belongs to a large group of zinc-based metalloenzymes that are known to catalyse the reversible hydration of carbon dioxide (CO₂ + H₂O ⇌ HCO₃⁻ + H⁺). The fastest human CA enzyme (HCA II) can hydrate at least 1.4 x 10⁶ molecules of CO₂ per second. At neutral pH and at slightly alkaline pH (ca. 8-9), this enzyme yields enzyme-bound Zn-OH⁻ (reaction 6) that is readily available to react with CO₂ (reaction 7) [7,8]. As a result, HCO₃⁻ ions formation is promoted (reaction 8) and the overall hydration rate of CO₂ is enhanced.

\[
\begin{align*}
E \cdot ZnH₂O & \leftrightarrow E \cdot ZnOH⁻ + H⁺ \\
E \cdot ZnOH⁻ + CO₂ & \leftrightarrow E \cdot ZnHCO₃⁻ \\
E \cdot ZnHCO₃⁻ + H₂O & \leftrightarrow E \cdot ZnH₂O + HCO₃⁻
\end{align*}
\]

The catalytic effect of CA enzyme on the kinetics of CO₂ hydration has attracted interest in the field of CO₂ capture and storage such as in gas separation [9] and in the field of CaCO₃ precipitation in aqueous brines [10]. This enzyme has been reported to generate a remarkable enhancement of the rate of CO₂ hydration and CaCO₃ precipitation under constant and slightly alkaline conditions (pH = 8-9). Nevertheless, the role of CA enzyme in lime mortar carbonation has not been explored yet. Different from pH-controlled systems, here we investigate the effect of CA enzyme on the reaction kinetics and phase transformations during carbonation of lime where the pH of the system continuously decreases from ≈12.5 to ≈8.2.

2. Materials and methods

CA enzyme from bovine erythrocytes in purified form was used. Saturated Ca(OH)₂ solutions without and with enzyme addition (0.6 μM) were subjected to carbonation in air (pCO₂ ≈10⁻³.⁵ atm at 20 °C). The solutions (150 ml) were maintained at a constant stirring rate (600 rpm) while continuously monitoring the pH.

In-situ phase transformations of CaCO₃ were investigated using a Jasco NRS - 5100 micro-Raman spectrometer equipped with a CCD detector and an integrated optical microscope (532.14 nm laser wavelength and 4 mW laser power). Micro-Raman images and spectra were collected in the frequency range 100-1200 cm⁻¹ at a spectral resolution 4 cm⁻¹. Carbonation was performed in air using a smaller volume of saturated Ca(OH)₂ solution (∼200 μl). In addition, in-situ precipitation of CaCO₃ was monitored with continuous acquisition of XRD patterns with Cu Kα radiation at 2θ range between 10 and 60° and at a scanning rate of 0.017 °/s, allowing the collection of a full diffractogram every ~2 min (Philips X’Pert Pro X-ray
diffractometer with Cu Kα radiation, \( \lambda = 1.5405 \) Å. CaCO₃ precipitates were examined using LEO Carl Zeiss GEMINI-1530 Field Emission Scanning Electron Microscope (FESEM).

Aged lime putty was used to follow up carbonation reaction in pastes and mortars under atmospheric conditions (20 °C; \( p\text{CO}_2 \approx 10^{-3.5} \) atm, RH ≥ 92%). Lime putty mortars were prepared in 1:3 lime putty to sand ratio by volume using standard mortar prisms (40×40×160mm) in accordance with EN 196-1. The mortars were cured at moist conditions (RH ≥ 92%) to assure the presence of moisture for CO₂ hydration and enzyme activity in the capillary pore solution of the mortar. The degree of carbonation was followed by thermogravimetric analysis (TGA) using a Netzsch STA 409 PC DSC-TGA system in static N₂ atmosphere at a T range of 20–1000 °C and at a controlled heating rate of 10 °C/min. Flexural and uniaxial compressive strength tests were carried out on mortar prisms at 14, 28, 90 and 180 days in accordance to EN 196-1.

3. Results and discussion

3.1 Kinetic effect of CA enzyme on the carbonation reaction

Figure 1 shows the evolution of pH as a function of time during carbonation under atmospheric conditions of pure and 0.6 μM CA-containing Ca(OH)₂ solutions. The overall trend of pH evolution clearly shows that carbonation takes place gradually. The starting alkaline pH values of the pure solution and CA-containing solution drop respectively from 12.4 and 12.6 to the final values of 8.2 and 8.3 when no further decrease is recorded, indicating the ending of the carbonation reaction.

![Figure 1. Evolution of pH of the pure Ca(OH)₂ solution and the one containing CA enzyme at 0.6 μM during atmospheric carbonation.](image)

Considering the reactions 3 and 4, the pH profiles in Figure 1 represent the evolution in OH⁻ ions concentration in the course of the carbonation reaction and thereby can be linked to the rate of CaCO₃ precipitation taking place in the solution. Two distinct stages are observed: (i)
an initial constant rate period with a change in the slope which is different for both solutions, and (ii) a subsequent falling rate period with an inverse S-shaped profile. Agnihotri et al. [5] reported that the major conversion to CaCO$_3$ (> 75%) occurs during the initial constant rate period. This implies that a large fraction of CaCO$_3$ precipitates during the constant rate period, and the falling rate period starting at pH ca. 11.83 corresponds to a nearly complete precipitation of CaCO$_3$. Calculations confirm this with that 97% and 99% conversions were reached at reaction rates of 0.1901 and 0.2426 mM L$^{-1}$ s$^{-1}$ for pure and CA-aided solutions respectively. The pH profiles clearly show that the carbonation reaction proceeds much faster in the presence of CA enzyme. This can be attributed to the presence of enzyme-bound Zn-OH$^-$ which promotes a faster supply of HCO$_3^-$ and CO$_3^{2-}$ ions to the solution as indicated in reactions 6-8. This is a strong evidence that CA enzyme promotes CaCO$_3$ precipitation in an alkaline solution where the pH of the system is continuously decreasing.

### 3.2 In-situ CaCO$_3$ phase transformations during carbonation reaction

Figure 2 shows the evolution of time resolved XRD patterns of the carbonating pure Ca(OH)$_2$ solution and the solution containing 0.6 μM CA to understand the kinetic effect that CA enzyme has on the phase transformations and on the final polymorph selection of CaCO$_3$. The first diffraction patterns represent the start of the carbonation reaction and indicates diffuse scattering with two broadened maxima between 20 and 50 °2θ. Such broad maxima are derived from the combined scattering from the aqueous solution as well as from the poorly-ordered ACC [11] which instantly precipitates as shown by micro Raman analyses (Figure 3).

Figure 2. Time resolved XRD patterns recorded during atmospheric carbonation of pure Ca(OH)$_2$ solution (left) and the solution with 0.6 μM CA enzyme (right).

The first detectable reflection in both solutions belongs to (10,14) calcite Bragg peak which started to emerge weakly embedded within the diffuse maximum at around 30 °2θ. This
corresponds to the onset of detectable crystallisation at ca. 144 min in pure solution while the waiting time decreases to 120 min in the presence of 0.6 μM CA. This justifies the enzymatic enhancement of CaCO₃ precipitation. Calcite is the only final crystalline phase precipitated irrespectively of the presence or absence of the enzyme.

In-situ micro Raman investigations have provided complementary findings on the instant phase formation of CaCO₃ and its transformations. Typical Raman spectra and photomicrographs of the observed phases in carbonating pure Ca(OH)₂ solution are presented in Figure 3. Silicon wafer, serving as the sample holder for the droplet of Ca(OH)₂ solution, is responsible for the diffuse Raman band at 994-922 cm⁻¹ and the sharp peak at 520.5 cm⁻¹ associated with Si-Si bonds. Upon air exposure, a mesh of spherical colloidal particles ≤ 1 μm in diameter formed instantly. Raman spectra of these spherulites typically show a major broad peak at around 1077 cm⁻¹ corresponding to the carbonate symmetric stretching (ν₁) and a broad featureless hump appearing as a continuous baseline rise in the low-frequency lattice region at 100-350 cm⁻¹. These spectral features imply lattice disorder (i.e. amorphous) of the carbonate group to which water molecules are hydrogen bonded [12]. This typically suggests that CaCO₃ is in the hydrated amorphous state as indicated by its spherulitic morphology which is characteristic of ACC [11]. Alongside these ACC clusters, micrometer-sized crystals precipitating nearly-simultaneously could be observed in the solution. Raman spectra of these crystals reveal two sharp peaks corresponding to internal vibration modes ν₁ (1082 cm⁻¹) and ν₄ (709 cm⁻¹), and two lattice vibration modes (280 and 155 cm⁻¹) that are typical for calcite [13]. Micro-Raman images showed the rhombohedral and prismatic morphology of calcite.

In the presence of CA enzyme, micron-sized spheres ACC formed instantly but its transformation to calcite occurred much faster than in the pure solution. Formation of vaterite was detected, which is known to transform from ACC, and it transformed to calcite via a dissolution precipitation mechanism. Interestingly, another type of large round particles (5 to 10 μm) appear in the form of isolated particles as well as chain-like aggregates (Figure 4). Their Raman spectra show a single ν₁ peak at around 1085 cm⁻¹ which is much sharper than the corresponding peak of hydrous ACC, and a weak ν₄ peak and lattice vibration modes. This implies that the environment of the carbonate group is more ordered than that of the hydrous...
ACC. This peak corresponds to a another ACC phase that has little or no structurally bound water and serves as a transient precursor in the formation of biogenic calcite and aragonite [12]. Our results suggest that anhydrous ACC is forming during lime carbonation in the presence of CA enzyme. Crystallisation of CaCO₃ in saturated Ca(OH)₂ solutions with and without CA enzyme under atmospheric conditions typically follows the Ostwald’s step rule [14]. Metastable ACC instantly precipitates and readily transforms into vaterite which then transforms into more stable phase of calcite via a dissolution/reprecipitation mechanism during carbonation reaction of lime [15,16]. In the CA-aided solutions, the transformation of ACC occurs much faster, the morphology of calcite crystals is significantly modified, and their size is remarkably increased due to the increased supply of HCO₃⁻ and CO₃²⁻ ions to the solution by means of the CA enzyme.

![Micro-Raman image](image)

Figure 4. Micro-Raman image (left) and spectra (right) of anhydrous ACC particles formed in carbonating Ca(OH)₂ solution with 0.6 μM enzyme. Scale bar on micro-Raman image: 5 μm

### 3.3 Carbonation in lime mortar

To verify the findings in saturated Ca(OH)₂ solutions, lime putty pastes were subjected to carbonation in air. Figure 5 represents the evolution of CaCO₃ precipitation in the carbonating pastes up to 180 days. Lime paste with CA enzyme mostly indicates higher contents of CaCO₃ precipitation than the pure lime paste. This justifies the kinetic effect of CA enzyme on lime carbonation in a porous system where the availability of CO₂ is diffusion related.

XRD analyses identified that the precipitates obtained at the end of the carbonation of pure lime paste and in the presence of CA enzyme are exclusively calcite as the final CaCO₃ phase. FESEM investigations support these findings. In pure lime paste rhombohedral and prismatic calcite crystals of nanometer size precipitated. In the presence of the enzyme, much larger rhombohedral calcite crystals precipitated. Appearance of new crystal faces suggests the modification of crystal habit from rhombohedron to “football” shape due to an interaction between CA molecules and specific calcite faces (Figure 6).
Figure 5. CaCO$_3$ precipitation in carbonating lime putty paste (LP) and with enzyme (CA).

Figure 6. FESEM images of calcite precipitated in the presence of enzyme. Scale bar: 500 nm.

Compressive and flexural strength results revealed higher values for lime putty mortar with enzyme than the pure lime putty mortar at all ages of testing (Figure 7). This finding evidences the enzymatic enhancement of carbonation reaction in lime mortar. Although the increment in the strength values is not more than 40%, the results are encouraging with respect to the effective role of CA enzyme in the enhancement of the reaction kinetics of lime mortar carbonation.
4. Conclusions

The effect of CA enzyme on the precipitation kinetics and phase transformations of CaCO$_3$ has been investigated with saturated Ca(OH)$_2$ solutions under atmospheric conditions. In pure solution, metastable ACC forms instantly and subsequently transforms to calcite and aragonite via vaterite. In the presence of CA enzyme, the crystallisation rate and the phase transformations from ACC to calcite occur much faster via intermediate phases of anhydrous ACC and vaterite. In addition, the morphology of the final stable CaCO$_3$ polymorph, that is calcite, is significantly modified while the particle size remarkably increases by the enzyme effect. This shows the enhancement of the carbonation reaction of Ca(OH)$_2$, and the preferential modification of crystal habit and morphology of CaCO$_3$ by means of enzyme-bound Zn-OH$^-$ which enhances the supply of HCO$_3^-$ and CO$_3^{2-}$ ions to the solution. Higher degree of CaCO$_3$ precipitation is recorded in lime paste aided with CA enzyme. This results in faster strength development in the mortar. These results are encouraging with respect to the effective role of CA enzyme in the enhancement of lime mortar carbonation.
References

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THERMO-HYDRO-MECHANICAL PROPERTIES OF REPAIR MORTARS DESIGNED FOR THE RESTORATION OF HISTORICAL BUILDINGS IN THE LOIRE VALLEY-FRANCE

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Abstract

Repair mortars used for restoration need to be highly compatible with historical materials in terms of physical, chemical and mechanical properties in order to preserve existing materials and to prevent early deterioration. In order to obtain the same physical, chemical and mechanical properties as Tuffeau stone (the historical stone from the Loire Valley Region of France), two mortars based on Tuffeau powder (waste from cutting operations) and on lime and fine silica sand were made (named F1 and F2 respectively). A third commercial mortar (V) was used as a reference material. The thermo-hydro-mechanical properties of these three mortars were studied and compared to that of Tuffeau stone. The results show that the porosity, the water absorption behavior and the thermal conductivity of the mortar (F2) were similar to those obtained with Tuffeau stone. The compressive strength, the tensile strength and the shearing strength of the two mortars were significantly lower than those obtained with Tuffeau stone, generally not exceeding 25%, showing that the mortar (F2) is softer than the original stone.

Recommendations are offered for using the Formula (F2) as a more compatible mortar that can be used in the restoration of monuments built of Tuffeau stone.
1. Introduction

In the cultural field, heritage is a property that, for various reasons, must be transmitted to future generations. Conserving, restoring and enhancing heritage buildings is thus a considerable economic and societal issue for scientific communities, and the search for innovative and appropriate solutions to the problems encountered is at the heart of the overall strategy of the sector. The principle of conservation is favored so as to allow lighter, cheaper operations and especially to guarantee the complete preservation of built heritage. Stone monuments are exposed to environmental conditions that may gradually induce significant degradation. Thus, a special strategy is needed for maintenance, conservation, repair, rehabilitation, and intervention measures [1, 2].

Degradation of stone materials under permanently open air conditions is mainly controlled by interacting chemical, physical and mechanical processes, leading to the destruction of the microstructure by degradation processes.

Repair mortars can co-exist alongside the replacement of stones: repair mortars are used when damage to the original material is limited, and replacement occurs when whole blocks or larger parts need to be restored. However, the borderline between when to use a mortar and when a replacement stone is required can vary greatly from one practitioner to another and even from country to country [3].

The building stone studied in this paper is Tuffeau, the limestone which was widely used in the construction of the famous castles of the Loire Valley in France. The stone’s whiteness and relative ductility and the fineness of its grains led to the completion of the elegant carved facades. White Tuffeau is a sedimentary rock of middle Turonian geological age of the Upper Cretaceous, 90 million years ago.

Tuffeau stones are machined from quarries and the blocks are then transported to the nearby processing plants. During this industrial process, the fine particle sand the water mix together, forming a colloidal waste. With increasing restrictions on landfills in nearby areas, the cost of waste disposal has increased accordingly and industries are forced to find ways to reuse the waste. Even though the reutilization of waste is already practiced, the quantity of waste reused in that way is still negligible.

Physico-chemical characteristics such as pore structure, microporosity, shrinkage and swelling of old mortars are very important with respect to the mechanical strength of a monument in restoration and conservation procedures. The pore structure is one of the main properties of mortars that greatly influences their permeability to water and water vapor, and strength, and is therefore a vital criterion of their compatibility. Compatible pore structures ensure the unhindered flow of water through the substrate–mortar interface, reducing the risk of creating a zone of damage due to ice or salt crystallization at the interface, which would affect the adhesive strength of a repair, and thus compromise its final compatibility. Repair mortars should not be more durable than the historic host material; their role should ultimately be sacrificial.

The requirements for building conservation regarding formulations for a repair mortar are mainly the hydraulicity of the binder, the mixture proportions (aggregate/binder ratio) and the
aggregate grading in order to identify the necessary components to produce a compatible mortar.

For several centuries lime-based mortars were used as binding materials in monuments. Several characteristics have been attributed to lime-based mortars: (i) slow setting that hinders and delays restoration work; (ii) lime mortars have lower strengths than cement mortars, and take longer to reach them. Cement-based mortars have therefore displaced lime-based mortars because of their faster setting, higher mechanical strength, advanced industrial development and affordable cost. In recent times, restoration interventions carried out using cement mortars have caused significant failures and acceleration of damage to monuments however, leading to the conclusion that cement-based mortars are unsuitable. Several studies of different binding materials have been carried out ([4], [5], [6], [7], [8] and [9]) in response to the reported objections to both lime and cement mortars. These materials should have the following characteristics: (i) chemical compatibility between the repair mortar and the old materials (stone or brick and their bedding mortar); (ii) physical compatibility, with special reference to the processes of solubility and water transport; (iii) structural and mechanical compatibility. One previous study stated specifically that a repointing mortar should be considerably weaker than the stone, and should deform significantly before failure. The use of some blended mortars could be interesting in this respect, because lime mortars with a certain amount of cement added might behave like hydraulic mortars, which are characterized by higher strengths than lime mortars, as well as a faster setting time, which improves their application [5, 10 and 11].

2. Scope of the research
In this context, and from a heritage and structural point of view, the restoration mortar must have a similar appearance and similar thermo-hydro-mechanical properties to the original building stone. The main scope of this study was to experimentally investigate the suitability of Tuffeau stone industry waste as a substitute material for fine aggregate in repair mortar production. This study also presents the design and comparative evaluation of these repair mortars based on the results obtained from the physico-chemical, mechanical and thermal properties of these mortars. The mortars were examined by microstructural measurements including scanning electronic microstructure while porosity was assessed by mercury intrusion porosimetry. Analyses of the drying shrinkage, mechanical and thermal properties were also conducted to ensure the reliability of using Tuffeau powder as a partial substitution in the mortar design and to ascertain the compatibility of these restoration mortars with the historical structures.

3. Experimental program
3.1 Materials
In this research work, three mortars were studied: two mortars based on lime, white cement, limestone powder and sand (F1 and F2) and an industrial mortar (V). The “F1” formula is characterized by a high mass ratio of binder (25% relative to the total mass) compared to the
“F2” formula (15%). To improve the adhesion between the mortar and Tuffeau stone, an adjuvant (Sika Viscobond) was added (3% of the binder mass).

The cement used in this study is a white cement CEM II / B-LL 42.5 R CE CP2 NF from the "Cruas" plant (chemical and physical properties are shown in Table 1). The lime is composed of 93% CaOH2. The solid skeleton of the two mortars is based on the limestone powder with a grain size between 0.5 and 100 microns (waste from cutting Tuffeau stone) and silica sand with grain sizes between 20 and 315 microns (Figure 1). The industrial mortar (V) is a repair mortar used for soft stone facades. It is made from limestone fillers, lime, a special hydraulic binder, and specific additives. As it is a patented product, no additional data can be given about its composition.

The fresh rock was extracted from an underground quarry at St-Cyr-en-Bourg (Maine-et-Loire, France). The main crystalline phases are calcite CaCO3 and silica SiO2. This limestone is a very lightweight building material, with a bulk density of 1.3 in its dry state for a total porosity of about 48% and a very large range of pore sizes (pore access diameters from 0.003 to 20 μm). Because of this high porosity, this building stone is a very soft stone with a compressive strength in the dry state of about 10 MPa.

Table 2 gives the composition of the two mortars. To obtain a better workability of the mortar, the initial water content was equal to the water content corresponding approximately to the liquid limit. Thus, the water/solid ratio was 0.4. After preparation of samples and before testing, the specimens were stored at 20 °C and at 75% relative humidity.

Table 1: Main characteristics of used materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tuffeau</th>
<th>Tuffeau Powder</th>
<th>Air lime</th>
<th>white cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineralogical composition (wt.%)</td>
<td>Calcite = 50% ; Opal CT = 30% ; Quartz = 10% ; Clay and Mica = 10%</td>
<td>Calcite = 50% ; Opal CT = 30% ; Quartz = 10% ; Clay and Mica = 10%</td>
<td>CaOH2 = 93% ; Calcite = 4.2% ; C3A = 11% ; C3S = 74% ; C2S = 12%</td>
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<td>Skeletal density (g/cm³)</td>
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<td>2.55</td>
<td>2.21</td>
<td>3.13</td>
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<tr>
<td>Bulk dry density (g/cm³)</td>
<td>1.31</td>
<td>0.85</td>
<td>0.38</td>
<td>-</td>
</tr>
<tr>
<td>Blaine surface (cm²/g)</td>
<td>-</td>
<td>-</td>
<td>11900</td>
<td>5300</td>
</tr>
<tr>
<td>Compressive strength (MPa) at 28 days</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td>Porosity (vol.%)</td>
<td>~ 48%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1. Grain size distribution for the sand and Tuffeau powder
Table 2: Mineral composition of the two formulations designed

<table>
<thead>
<tr>
<th></th>
<th>sand</th>
<th>Tuffeau powder</th>
<th>binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>38 %</td>
<td>37 %</td>
<td>25 % (2/3 lime + 1/3 white cement)</td>
</tr>
<tr>
<td>F2</td>
<td>43 %</td>
<td>42 %</td>
<td>15 % (2/3 lime + 1/3 white cement)</td>
</tr>
</tbody>
</table>

3.2 Methods

The Vicat setting time was measured according to the NF EN 163-3 standard. The heat flow of the reaction was measured using a TAM Air® isothermal microcalorimeter. The heat flow was measured on a 20g mass of binder during 72 hours.

Capillary water absorption was measured according to the EN-1925 (99) Standard. Previously dried cylindrical samples were placed in a hermetic tank, at the bottom of which the distilled water level was maintained constant during the entire period of the test. The mass of wet samples was measured as the height of the advancing capillary front at increasing intervals of time, using vernier calipers.

Drying shrinkage was measured according to the NF P15-433 standard. A retractometer was used to measure the shrinkage of prismatic samples (4x4x16 cm³). The tensile and compressive strength tests were carried out at 28 curing days, on prismatic samples measuring 4x4x16 cm³ according to EN 1015-11 (99). The shear strength was measured with a Casagrande box used in soil mechanics. The sample was placed between two halves of the box which are movable relative to each other. The lower half-box was driven horizontally at a constant speed of 0.5 mm/min (Figure 2). The upper half-box was fixed and connected to a load ring to measure the forces in the shear plane. The maximum tangential force measured can be compared to the failure shear stress if the failure plane orientation in the shear axis is verified. Moreover, vertical pistons apply normal stress on the shear plane of the sample in order to study the friction behavior of the stone-mortar interface. The sample used was cylindrical in shape and had a diameter of 4 cm and a height of 4 cm (2 cm of mortar adhering to 2 cm of Tuffeau in the case of assemblies). All samples were tested in the saturated state.

Thermal conductivity was measured using a FP2C: this is a device for instantaneous measuring of thermal conductivity and effusivity. The principle is based on a local thermal disturbance via a small variation in the temperature of the material (a few degrees above ambient temperature).
Finally, thermal expansion was measured on samples exposed to three different temperatures (20 °C, 40 °C and 60 °C). Each temperature was maintained for 24 hours before measuring the deformation. In this test, the samples were protected with plastic film to avoid drying.

4. Results and discussion

4.1 Hydration and microstructure

Figure 3 shows the evolution of heat flow vs. time. The release kinetics of the thermal flow shows that the mortar "V" has a large exothermic reaction with a first peak at about 8 hours followed by a second peak at about 15 hours of curing. Regarding the mortars containing the Tuffeau powder, the mortar “F1” has a larger peak than the mortar “F2”. This finding can be explained by the amount of binder which is greater in the “F1” formula, which consequently contains a larger quantity of cement. For the F1 mortar, the peak appears at 9 hours of curing against 14 hours for the formula “F2”. From these findings we can classify the three mortars by order of reactivity: the most reactive mortar is the mortar “V” followed by the mortar “F1” and then “F2”. These heat flow release results are consistent with the results of Vicat setting time. As can be seen on Figure 4, the mortar "V" sets faster than the other two mortars; it starts at 8h and finishes at 26 h. For the “F1” mortar, setting starts at 10 hand ends at 34 h, while the mortar “F2” has the slowest setting time, starting at 12 and finishing at 40 h.

![Figure 3. Heat flow for mortars](image-url)

![Figure 4. Vicat setting of different mortars](image-url)

![Figure 5. Pore size distribution for different mortars](image-url)

![Table 3: Total porosity for mortars](image-url)

<table>
<thead>
<tr>
<th>Material</th>
<th>Total porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>29</td>
</tr>
<tr>
<td>F1</td>
<td>43</td>
</tr>
<tr>
<td>F2</td>
<td>47</td>
</tr>
<tr>
<td>T</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 3: Total porosity for mortars

Figure 3. Heat flow for mortars

Figure 4. Vicat setting of different mortars

Figure 5. Pore size distribution for different mortars

Figure 5. Shows the results obtained by the mercury intrusion porosimetry (MIP) test. The mortar "V" has the finest pore network with two peaks at 0.5μm and 1.7μm, respectively,
followed by mortar "F1" which has a slightly coarser structure with the presence of two peaks at 2.2µm and 1.2µm, respectively. The mortar "F2" has a single pore structure centered on 1.5µm. The pore sizes of the three mortars are much lower than the pore size of Tuffeau stone which is located at 8µm. The total porosities measured by MIP were 29%, 43%, 47% and 48% for the mortars "V", "F1" and "F2" and Tuffeau stone, respectively. Hence in terms of total porosity, the mortar "F2" is more compatible with Tuffeau stone. Figure 6 shows the texture of the three mortars studied at 28 days of curing. The three mortars have almost the same color (creamy white) similar to the color of Tuffeau stone. It is also important to note that no cracks (or microcracks) were observed. The development of cracks is a frequently encountered problem in the formulation of such products [5, 12, 13, 14 and 15].

4.2 Mechanical properties
Table 4 presents the results of mechanical tests of the three mortars, those of Tuffeau stone and the shear strength of the mortar-Tuffeau stone composite. The samples used for mechanical characterization were stored at a temperature of 20 °C and at a relative humidity of 75%. The results of the compressive strength and tensile strength tests showed a low strength of the three mortars compared to that of Tuffeau stone. The mortar F2 had the lowest compressive and tensile strength values (1280 kPa to 270 kPa, respectively). Low mechanical strength can be an advantage in the preservation of historical monuments as it results in an accumulation of damage in the repair mortar, leaving the original material (often the stone) in...
sound condition. The study of the stone-mortar interface via direct shear tests using the Casagrande box showed good adhesion at the interface. The shear strength value obtained was close to that of the different mortars and very different from that of Tuffeau stone. This finding is very important: the developed mortars show an acceptable adhesion to stone and at the same time applying a strong shear stress causes failure in the mortar and not in the stone.

The shear strength of the interface mortar "F2"-Tuffeau stone (F2-T) was the lowest of the three assemblies (530 kPa). According to the study related to the mechanical strength, it is clear that the three mortars are mechanically resistant but the mortar “F2” contributes most to the preservation of the original stone.

Table 4: Mechanical characterization of the different materials

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>F1</th>
<th>F2</th>
<th>T</th>
<th>V-T</th>
<th>F1-T</th>
<th>F2-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear strength (kPa)</td>
<td>672</td>
<td>650</td>
<td>470</td>
<td>1933</td>
<td>730</td>
<td>615</td>
<td>530</td>
</tr>
<tr>
<td>Compressive strength (kPa)</td>
<td>1940</td>
<td>1630</td>
<td>1280</td>
<td>7120</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength (kPa)</td>
<td>430</td>
<td>380</td>
<td>270</td>
<td>1240</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 8 shows the results of drying shrinkage versus time. The resulting curves have two phases:

- a first phase from the casting to the beginning of setting (between 8 and 12 hours); this is the phase of Le Châtelier contraction due to the formation of hydrates which causes a decrease in the total volume;
- a second phase of drying shrinkage, which starts at the beginning of the setting, and then stabilizes after 35 hours approximately.

This figure also shows that the mortar “F2” has low shrinkage values not exceeding 400μm/m at 28 days. For the “F2” Formula, shrinkage begins to stabilize immediately after the onset of setting. The low shrinkage of the "F2" mortar means a low deformation in the stone-mortar interface and therefore less risk of interface failure.

4.3 Hydraulic and thermal properties

The imbibition properties of mortar are directly related to the size and shape of the pores and the connectivity of the porous network. For this test, samples of mortar (diameter: 50 mm/ height: 50 mm) were placed in a sealed tank with a constant water level in the bottom.
At different times, the samples were weighed and the capillary front height was measured by calipers until saturation. The evolution of the capillary front height according to the square root of time of the different mortars and stone is shown in Figure 9. For the various mortars, these curves have a linear shape, demonstrating the homogeneity of their porous networks. The slopes of these curves define the imbibition coefficients. In this figure, we see that the rate of water front propagation of the mortar F2 and Tuffeau stone are almost identical. This rate decreases for "F1" and "V" mortars. A difference in capillary front propagation between the mortar and the stone may cause crystallization of salt in the stone-mortar interface.

![Figure 9. Imbibition test for different mortars](image)

The thermal dilation and thermal conductivity of the materials are presented in Figure 10. It can be seen that the thermal conductivity of Tuffeau stone is similar to those of the formulas “F1” and “F2” which are 0.52 W/m.K, 0.4 W/m.K and 0.44 W/m.K, respectively. Mortar "V" has a relatively high thermal conductivity of 0.8 W/m K. Regarding thermal dilation, Tuffeau stone and mortar "F2" exhibit similar thermal expansion values 7.9x10⁻⁶ µE/°C and 7.76x10⁻⁶ µE/°C against mortars "V" and "F1" whose thermal dilation is different from that of Tuffeau stone, with values of 9.6x10⁻⁶µE/°C and 6.4x10⁻⁶µE/°C for the mortar "V" and mortar "F1", respectively.

5. Conclusion

In this study on the development of a compatible mortar for the restoration of Tuffeau stonework, two mortars were developed and compared to a commercial mortar as a reference. The results can be summarized as follows:

- The formulation of a sand and Tuffeau powder based mortar (with the compositions used here) gives a mortar with a similar color to that of Tuffeau stone (creamy white),
- The use of small amounts of cement in the formulation and suitable curing conditions prevented cracking in the developed mortars,
- The developed mortars have a total porosity similar to that of Tuffeau stone. This property is responsible for a thermal and hydric behavior of the two formulas "F1" and "F2" that is similar to that of Tuffeau stone,
- The low mechanical strength obtained for the developed mortars allows them to absorb the applied stresses and leave the original stone in sound condition,
Finally we note that the drying shrinkage and thermal expansion of the formula “F2” makes it more compatible with Tuffeau stone.

References
DURABILITY OF AIR LIME MORTAR

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Technical University of Denmark, Lyngby, Denmark

Abstract
This contribution deals with the physical and chemical reasons why pure air lime mortars used in masonry of burned bricks exposed to outdoor climate have shown to be durable from the Middle Ages to our days. This sounds strange in modern times where pure air lime mortars are regarded as weak materials, which are omitted from standards for new masonry buildings, where use of hydraulic binders is prescribed. The reasons for the durability seem to be two:
1. The old mortars have high lime contents.
2. The carbonation process creates a pore structure with a fine pored outer layer and coarser pores inside. This difference in pore size will delay the capillary suction of rain from outside, while excess water inside can be sucked to the front and evaporate.

1. The high lime contents

The lime contents of mediaeval mortars are high, 25 - 40 % [1]. The reason for this fact is that the mortars were produced by the so-called hot lime technic. The burned lime (CaO) were mixed with gravel and water, and so it slaked to calciumhydroxid (Ca(OH)₂), ready to be placed in the building. (Lime mortar produced by wet slaked lime (kulekalk) can be produced with 13 % lime as maximum, because of the high water content of the lime dough.)

The carbonation of such lime rich mortars takes time, the higher the lime content and the thicker the wall, the longer the time. You can find very thick old walls, where the mortar is still uncarbonated after hundreds of years. Meanwhile, although the mortar is not carbonated, the load bearing capacity of the wall is present immediately after the construction. This is due to the capillary action in the pore water: During the brick laying the tiles suck up the excess water from the mortar. In this way a hydraulic under-pressure is created in the water. At moisture equilibrium at 80 % RH, 20 °C, the under pressure in the water is about 20 MPa.
This pressure secures the tiles in their places and forms the skeleton in the gravel to its load bearing duty. So, water is the binder in this situation, until the carbonation has taken place.

The load bearing effect of the water has been shown in experiments on our institute [6]. The cohesion of mortar in joints between two tiles was measured in a torsion test [7]. E.g. in a 9% air lime mortar the cohesion after 28 days was 0,17 MPa, while the value after 16 weeks, where the joints were fully carbonated, were 0,14 MPa.

2. The pore structure

When both calcium hydroxide and carbon dioxide are available, the carbonation process (Ca(OH)$_2$ + CO$_2$ = CaCO$_3$ + H$_2$O) is a relative fast process. This can be seen on the surface of freshly poured limewater in a bucket. In less than a quarter of an hour a grey layer has been created. It consists of very small crystals of calcium carbonate reflecting the light. The crystals can be seen in polarised light (Figure 1). During a week the crystal layer gets a thickness of 0.03 – 0.04 mm.

![Figure 1. Carbonation on the surface of limewater. Crystals can be seen in the microscope.](image)

This creation of small calcium carbonate crystals also takes place rather fast on the surfaces of freshly placed joints or plaster. (Von Balen et al [2] have shown that the take up of carbon dioxide in a mortar joint is two to three times faster in the first five minutes than after five hours.) The small crystals form a continuous layer on the surface. The carbon dioxide can still penetrate this layer and continue the hardening in the inner parts of the mortar. The final result is that we get a structure with a surface layer with much smaller pores than the bulk mortar (Figure 2).

![Figure 2. Cross-section of the outer layer of a 12 % lime mortar. Fluorescent light.](image)
It is well known from the physics that a capillary tube with a small diameter is able to suck water from a tube with larger diameter, while the opposite cannot take place. For a mortar joint with a pore structure as described above this means that the suction of rainwater from outside is delayed in relation to the suction in a mortar without a crystal layer. On the contrary, an excess amount of water in the internal part of the joint will be sucked to the surface and evaporate. One can say that the mortar joint acts as a hygrodiode. The positive effect of lime coatings on drying is shown in [9].

The effect can be seen on a piece of mortar from the outside of a joint. If water is dripped on the surface exposed to the weather, the water will lay as a pearl on the surface. If you turn the piece around and drip from the backside, the water is sucked up directly. In Figure 3 the effect is shown on a horizontally placed joint, where the surface layer has been damaged in two places.

![Figure 3](image_url)

**Figure 3.** Joint of a 12 % air lime mortar placed horizontally. The mortar is of the same kind as shown in Figure 2. Three water drops are placed.

One may object that the surface layer will be dissolved by acid rain. This is correct, but it must be taken into consideration that the mortar joint is not a static system, where nothing more happens, when the first carbonation has taken place. Matter is transported back and forth in the pores. Calcium ions from the inner uncarbonated part of the joint may diffuse and meet carbon dioxide diffusing from the air. Anyhow, the surface layer continues to be there, as it can be seen on thin sections of old mortars. These transportation phenomena ought to be studied to increase our understanding of the influence of lime content and weather conditions on the thickness of the surface layer.

White wash and rendering with air lime mortars carbonate in the same way as described above. So the effect as a hygrodiode is also present in these structures. Limewater, which is a saturated solution of calcium hydroxide, Ca(OH)$_2$, is often used as the last treatment of lime washed surfaces or renderings. (The solubility of Ca(OH)$_2$ is 0.16 g per 100 ml water at 23 °C.) The effect of this treatment is to thicken the crystalline surface layer. The outermost Ca(OH)$_2$ carbonates on the surface, and as the concentration of the Ca(OH)$_2$ decreases, new Ca(OH)$_2$ is drawn against the surface and carbonates there. The use of limewater is analysed and recommended in [8].
3. The church tower case

A case of damage shall be mentioned here as an illustration of the importance of the lime content and the surface layer. The church in Kirke Værløse had its tower built between 1400 and 1450. The mortar was produced as hot lime mortar and had a lime content of 25 - 40%. The original joints in the least exposed parts of the tower are still intact. In 1994 - 1998 the joints in the top of the tower were repaired. The medieval joints were removed to a certain depth by milling, and new material placed instead. One was aware that an air lime mortar should be used, but the lime content was obviously not considered, as a mortar with 6,6% lime was used (!)

Figure 4. The church tower in Kirke Værløse.

Left: Both the tiles and the mortar in the top part were severely damaged by frost action. Middle: Section of medieval mortar. See Figure 5. Right: Section of the 6,6% repair mortar. Both micrographics: Transmitted light. No filters. Top of the picture is the outside surface. Dark colour is lime binder. (Photo: SEIR-materialeanalyse A/S)

Figure 5. Enlargement of the section of the medieval mortar. The “R’s” show cracks. Transmitted light. No filters. Dark colour is lime binder. Top of the picture is the outside surface with the dense calcium carbonate layer. (Photo: SEIR-materialeanalyse A/S)
After ten years the top of the tower suffered from severe frost damages, which turned the colour of the top from brownish to light red, as the outer layer of the tiles disappeared. A 6.6% mortar has not enough lime to fill the space between the gravel particles and the surface layer is not sufficient to avoid water penetration, cf. Figure 4. In 2009 - 2015 the joints were repaired again with a mortar developed by master bricklayer Ole Jensen containing 25% lime produced as hot lime.

4. Capillarity

The mortars from Kirke Værløse and Farum churches were included in a project, where the moisture properties of different air lime mortars were examined [3]. The capillary suction capacity was measured by means of the so-called Karsten tube.

Figure 6. The 25% mortar developed by Ole Jensen was also used by the repair of a wall around the churchyard at Farum church. Picture is taken during measuring of capillarity with the Karsten tubes. (Photo: Martin Jensen)

The coefficients of capillarity were calculated from the measurements by means of a method invented in [5]. In laboratory measurement were taken on platen of 6.6%, 9% and 13.5% air lime mortar. Specimens of the in Denmark very common used lime-cement mortar KC50/50/700 (50 kg air lime, 50 kg Portland cement, 700 kg sand) were included for comparison. The results are seen in Table 1 and Figure 5. In a textbook [4] the coefficient of capillarity for lime mortar can be read as 0.25 kg/m²s¹/² and for concrete to 0.01 - 0.3 kg/m²s¹/².

Measurement of capillarity is a tool in the evaluation of the frost resistance of the mortars. Porous building materials are frost-resistant as long as the water saturation degree, $S$, is lower than the critical degree of water saturation, $S_{krit}$, for the material in question. The reason why the medieval air lime mortars are frost-resistant seems to be that the combination of the high lime content together with the fine crystalline surface layer is able to keep $S < S_{krit}$. In the church tower case mentioned above the lime content in the old mortar was good, while 6.6%
lime was not enough to secure against frost damage. This finding coincides with the capillarity seen in Table 1 and Figure 5. Which lime content is enough to secure frost resistance should be cleared out in further research.

Table 1: Coefficient of capillarity of lime mortars [3]. To the right is shown the Karsten tube.

<table>
<thead>
<tr>
<th>Mortar type</th>
<th>Coefficient of capillarity, kg/m²s^{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,6% Kirke Værløse church</td>
<td>0,38</td>
</tr>
<tr>
<td>6,6% Laboratory specimens</td>
<td>0,41</td>
</tr>
<tr>
<td>9,0% Laboratory specimens</td>
<td>0,28</td>
</tr>
<tr>
<td>13,5% Laboratory specimens</td>
<td>0,16</td>
</tr>
<tr>
<td>KC 50/50/700 Lab. specimens</td>
<td>0,12</td>
</tr>
<tr>
<td>25% Farum church</td>
<td>0,01</td>
</tr>
</tbody>
</table>

Figure 5. Coefficient of capillarity of air lime mortars. Measured by means of the Karsten tube. The white mark is the result from the very common lime-cement mortar KC50/50/700. From [3].

5. Discussion

The protecting effect from the inhomogeneous pore structure occurs not only in pure air lime mortars. Mortars with hydraulic binders containing a certain amount of air lime also create the crystalline surface layer of calcium carbonate. In [3] it is seen on a thin section of a KC50/50/700 mortar. How much “a certain amount of air lime” is needs more research to be cleared out. - A practical example of the durability of a lime-cement mortar is seen on the yellow masonry buildings on DTU, which were erected in 1963 - 1971 using a mortar much like KC50/50/700. To my knowledge now frost damages have been reported.
The hardening of a pure cement mortar is quite different from the hardening of a lime mortar: Firstly after the brick is placed the tiles suck up the excess water, and the tiles are kept in place by the under-pressure in the water. During the following hours the mortar sets in bulk. The hardening continues in the whole volume during the next days and months. This gives a homogeneous microstructure in the whole volume. Further, the pores in the hardened cement binder are much smaller (10 - 100 nm) than the pores between the carbonate crystals in the lime mortar (100 - 1000 nm). The homogeneity and the smaller pores in the cement mortar will give a worse drying potential to the surroundings, as related to a lime mortar. Maybe a surface layer is created as the cement-binder carbonates, but the pore size may be of a magnitude, which cannot draw water from the fine pores in the binder. More research is needed to elucidate the connection between pore structure and the drying potential and the effect that additives have on this.

6. Conclusion

Air lime mortar in joints and rendering exhibits a good frost resistance in spite of the rather poor mechanical strength. This is due to a certain amount of binder and to an inhomogeneous pore structure, where a surface layer of fine calcium carbonate crystals acts as a hygrodiode, which keeps the coarse pored bulk material dry, and in this way protect the structure from frost damage. - More research is needed to elucidate the phenomenon.

Acknowledgement

Wewers Mørtel A/S kindly supported the projects behind [3] and [6].

References

[1] Hansen, H. and Dam, H., The mortars of the middle ages, Danish Technological Institute, Aarhus (2009)
EFFECT OF APPLICATION OF LIME PLASTERS TO SALT-LADEN BRICKS

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(1) Institute of Theoretical and Applied Mechanics, Prague, Czech Republic

Abstract

Historic masonry is usually contaminated with soluble salts that change the properties of the original materials. The design of mortars for historical repairs should, therefore, take this condition into account. The aim of this study is to investigate the performance of lime plasters cured on a salt laden substrate. A lime mortar (L) and a lime mortar with a traditional hydrophobic admixture (LO) were applied to sodium sulphate laden bricks, and the properties of the plaster/brick systems were examined after curing. The results indicated that L mortar works as a salt-transporting plaster, whereas LO functions as a salt-blocking plaster and the salt accumulates preferentially at the interface between the plaster and the brick. The capillarity curves showed that the hydrophobic effect of LO plaster was significantly affected despite the small amount of salt that migrated from the brick to the plaster during curing. No change in the water absorption kinetics was observed for L plaster cured on a salt-laden brick and the drying process was only slightly altered while it extracted more than 50 wt.% of the salt initially present in the brick. In contrast, the hydrophobic plaster significantly reduced the drying rate in both salt-free and salt-contaminated bricks.

1. Introduction

The presence of moisture and soluble salts in historic masonry is a common conservation problem in architectural heritage. Mortars applied either as bedding plasters or renders play a very important role in the moisture and salt transport. Generally, mortars are the building materials firstly affected by weathering agents, and more often must be repaired or substituted. Porous building materials contaminated with salts have a different thermodynamic and mechanical behaviour than the sound materials. Therefore, the formulation of a repair mortar must be compatible with the original materials while addressing the weathering contaminants accumulated throughout its service life. Laboratory
salt resistance studies performed in mono-material mortar samples are very common [1-4]. Fewer but enlightening studies have been published with a combination of materials [5-7]. Studies focusing on the performance of repair mortars applied on salt laden substrates are a more recent and less studied subject [8, 9].

Water-repellent mass additives are often used in plasters/renders to minimise salt dampness and surface damage by salt crystallisation [8]. According to Lubelli and Rooij [9], depending on the effectiveness of the water-repellent and on where the water-repellent is present (in the entire plaster or only in the outer layer), the salt will accumulate either at the substrate/plaster interface or in the inner part of the plaster system. The current conviction for the use of hydrophobic substances in plasters or renders for salt-loaded masonry is that a lower water absorption coefficient will hinder the transport of liquid solutions to the outer surface, thereby preventing or reducing the occurrence of surface damage. However, there is field evidence that surface damage can be worsened, rather than minimised, when partially hydrophobic plasters or renders are used [10].

Groot et al [11] state that the more the plaster restricts the transport of moisture and salt to the surface, the higher the risk of damage to the surrounding old materials. However, given the results previously obtained [12] on the properties of standard mould mortar specimens with the addition of linseed oil as an hydrophobic admixture (in the mortar bulk), namely in the effect on drying and vapour transport, we found important to study the same type of mortars applied as plasters on brick and salt-contaminated brick. The aim of this study is to investigate the performance of lime and hydrophobic lime plasters cured on a salt laden substrate.

2. Experimental part

2.1 Materials and sample preparation

The mortar mixtures were prepared with lime (class CL90) and river sand (grain size 0-4mm). The binder:aggregate ratio was 1:5wt. (1:1.5v). The amount of linseed oil, water:binder ratio and air content of the freshly mixed mortar [13], the average of 3 measurements, is given in Tab 1. The amount of kneading water added to the mixtures aimed to achieve a consistency of ca. 145-150mm ø measured with the flow table [14]. The mixing process is described in [12].

<table>
<thead>
<tr>
<th>Mortar code</th>
<th>Oil amount (wt.%)</th>
<th>Water:binder ratio</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-</td>
<td>1.02</td>
<td>3.3 (±0.14)</td>
</tr>
<tr>
<td>LO</td>
<td>1.5</td>
<td>1.11</td>
<td>4.6 (±0.14)</td>
</tr>
</tbody>
</table>

Fired-clay bricks were used as the substrate; the bricks were cut into prisms of ca. 30×50×50mm and dried at 60°C to constant mass. One group of bricks were salt laden by immersion in a 7 wt.% thenardite solution (Na2SO4) at room T for 48h, and another group was immersed in pure water. The amount of water and salt solution absorbed by the bricks was 13.7 (±0.6) and 14.1 (±0.6) wt.% (average of 8 specimens), respectively. Then the mortars
were applied on one of the 50×50mm brick surfaces. This way of preparing the specimens leads to an homogeneous distribution of salt in the brick, but in practice, the salt is usually heterogeneously distributed. However, conclusions can be drawn about the effect of the presence of a high concentration of dissolved salt on the properties of the plasters after curing and contribute to explaining the occurrence of localised damage often observed in the field. The amount of salt introduced into the brick specimens amounts to ca. 1wt.%, which corresponds to an extremely high sulphate content (> 0.77 wt.%) according to EUREKA EU-1270 [15]. The thickness of the plaster layer was ca. 0.8-11mm. The specimens prepared with the bricks contaminated with salt are designated as L/S and LO/S for lime and lime with oil, respectively. The specimens prepared with bricks that were immersed in water instead of salt solution are identified as L/R and LO/R for lime and lime with oil plaster, respectively. After preparation, the samples were stored at ca. 90% relative humidity at room temperature for eight days. Afterwards, the side surfaces were sealed with epoxy resin, and the samples were placed in a CO2 chamber (6 wt.%) with 60±5 % RH and 25±5ºC for 60 days with the plaster layer facing up. Standard mortar specimens 160×40×40mm in size were also produced with the same composition to compare the properties of the mortars cured over brick, here designated as plasters, with the standard mortar specimens, here designated as mould mortar and identified as L/M and LO/M, for lime and lime with oil, respectively. Both mould mortar and plaster/brick systems were prepared on the same day and cured in the same chamber.

2.2 Methods of analysis

One thin section of each plaster/brick system was impregnated under vacuum with epoxy resin and then observed with an optical microscope (OM). The mineralogical composition of the plaster binder rich fraction was studied by X-ray diffraction (XRD) with one sample of each plaster (salt-free and salt-contaminated; the quantitative phase analysis was done by the Rietveld method. The pore size distribution (PSD) was investigated with a mercury intrusion porosimeter with three samples of each material.

The water absorption by capillarity test [16] was performed with four specimens of each material. Both exposed surfaces of the plaster/brick specimens were tested, i.e. one group of four samples was placed with the plaster surface in contact with water, and another group was placed with the brick surface in contact with water. Both salt-free and salt-contaminated specimens were tested. The salt-contaminated specimens were tested individually in a Petri dish. When the specimens were saturated, the group of four samples tested with the plaster surface in contact with water were used for the determination of the evaporation curve [17]. Thus, one must take into account that the drying test was carried out after wetting the specimens; wetting can have resulted in hydration pressure from mirabilite (Na2SO4·10H2O) precipitation, which can consequently affect the pore-network and alter the drying rate. The samples were placed in a room with controlled T and RH (20°C and 40%). The characterisation of the evaporation was performed by the determination of the drying coefficient and the drying index [18]. The salt efflorescences formed were collected at the end of the drying test, dried at 60ºC, and weighted to determine the amount of salt exuded. The quantity of salt is slightly underestimated because, during the absorption of water by capillarity, diffusion of dissolved ions toward the source of invading water occurs. The quantification of the amount of salt dissolved that remained in the Petri dish after the water absorption by capillarity test amounted to a quantity lower than 1 wt.%.
3. Results and discussion

3.1 Microstructure and composition of the plaster/brick systems

After the curing period, the surface of L/S plaster showed a thin layer of salt efflorescences and moisture stains, indicating that salt migrated to the plaster during curing. The plasters prepared with oil (LO/S) did not show visually detectable alterations with respect to the reference (LO/R). Fig. 1 shows OM images of the thin sections of L/S and LO/S plaster/brick specimens. The fact that the plasters were applied to the brick right after the immersion period, without allowing the salt to precipitate, has probably contributed to the good plaster/brick adhesion observed, analogous to the salt-free specimens. Both the salt-free and salt-contaminated plasters showed extensive cracks (ca. up to 30\(\mu\)m in width) probably assigned to shrinkage phenomena, thus being more intense close to the evaporation surface. Moreover, during the bonding process, particles of binder will be transported towards the bond plane; hence, the mortar becomes more compact near the interface [19]. The extent of cracks in LO is lower compared with L, probably owing to the presence of spherical pores (5 to 30\(\mu\)m \(\phi\)) related to the high air content of the fresh mix.

The thin sections of the salt-contaminated specimens show where salt precipitated during curing. The use of water during the polishing procedure can have dissolved some of the salt, thus, the concentration of salt could be even higher. Plaster L/S showed a porous structure similar to L/R, but the surface exhibited a white layer of 5-10\(\mu\)m thickness covering most of the surface (Fig.1.a). This layer is probably constituted by salt that migrated from the brick to the plaster during curing, as could be visually observed by the naked eye. Salt also crystallised at the interface between the brick and the plaster (Fig.1.b). The accumulation of salt at the interface occurred only in two confined areas of the analysed specimen, and it is probably related to the existence of interfacial zones with a distinct permeability. In the case of LO/S, there was accumulation of salt along the entire interface (Fig.1.d). This is probably related to the fact that liquid transport is not possible across the hydrophobic layer, and water evaporates mostly beneath the plaster, which is in line with the literature [9].

Figure 1. OM images of the thin sections of salt-contaminated plaster/brick specimens: a,c) top of the plaster; b,d) brick/plaster interface. The arrows indicate salt accumulation.
subflorescence forms at the interface between the two materials, which can eventually lead to detachment of the plaster [8].

The binder-rich fractions of the plasters were analysed with XRD and the results of the quantitative phase analysis are presented in Tab. 2. A small amount of portlandite was detected in LO samples, even after the artificially induced carbonation, indicating that the presence of oil hinders the carbonation reaction, confirming previous results obtained with TG-DTA in standard mortar specimens [12]. Thenardite was detected in a much higher amount in L/S than in LO/S, which is in line with the OM observations. No other phases related to the presence of sodium sulphate were detected. Besides calcite, portlandite and thenardite, all the other mineral phases identified (e.g. quartz, muscovite, albite) concern the composition of the aggregate.

Table 2: XRD quantitative phase analysis (in %) of the binder rich fraction of the plasters cured on a salt-free and salt-contaminated brick (n.d. - not detected).

<table>
<thead>
<tr>
<th>Mineral phases</th>
<th>L/R</th>
<th>L/S</th>
<th>LO/R</th>
<th>LO/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>14.6 ±0.2</td>
<td>18.4 ±0.2</td>
<td>39.9 ±0.2</td>
<td>23.7 ±0.2</td>
</tr>
<tr>
<td>Portlandite</td>
<td>n.d.</td>
<td>n.d.</td>
<td>3.7 ±0.1</td>
<td>2.0 ±0.1</td>
</tr>
<tr>
<td>Thenardite</td>
<td>n.d.</td>
<td>1.4 ±0.1</td>
<td>n.d.</td>
<td>0.1 ±0.0</td>
</tr>
</tbody>
</table>

3.2 Properties connected with the movement of water

Fig. 2 shows the pore size distribution (PSD) curves of the brick and plasters cured on salt-free and salt-laden bricks. The maximum pore access radius in bricks is unimodal showing the pore volume maxima around 1.6μm. Plaster L/R shows a bimodal PSD with a sharp main peak centred at ca. 0.7μm, and a second broad peak in the macropore region centred at ca. 20μm. Plaster LO/R also shows a bimodal distribution with the main pore size centred at ca. 0.8μm, and a second broad peak also centred at ca. 20μm. The pores detected in the macropore region are probably assigned to shrinkage cracks, which is in line with the OM observations. The PSD is not much altered in plasters cured on a salt-laden brick.

The water absorption by capillarity curves of the salt-free and salt-contaminated systems are shown in Fig. 3. Plaster LO/S showed a remarkable difference in the rate of water absorption.
compared with LO/R. The results indicate that the hydrophobic properties of LO are significantly affected when the mortar is cured on the salt-laden substrate, even though a very small amount of salt migrates to the plaster during curing, as determined by XRD (Tab. 2). In contrast, L mortar showed negligible difference in the rate of water absorption by capillarity between the plaster cured on salt-free and salt-laden brick. These results indicate that the active capillary pores of L plaster are not affected by the salt contamination from the brick.

Figure 3. Water absorption by capillarity curves of the plaster/brick specimens: a) plaster surface in contact with water, b) brick surface in contact with water.

The salt-contaminated samples tested with the plaster surface in contact with water did not show visual alterations after the capillarity test. The specimens with the brick surface in contact with water showed degradation of the plaster surface. Fig. 4 shows the aspect of the samples after the water absorption test; LO specimens exhibited slight surface powdering and scaling; LO mortar layer was severely cracked. The observed alterations are probably related to the dissolution of thenardite and reprecipitation as mirabilite, the resulting damage being due to the crystallisation pressure exerted by mirabilite [20]. The cracks observed in LO/S are possibly assigned to the high pressure developed between the growing mirabilite crystals and the hydrophobic pore wall. According to Scherer [21], if the contact angle between a crystal and the pore wall is lower than 90°, then the stress in the pores can be small, as in the case of L plaster and brick; if the contact angle is higher than 90°, as in the case of LO, crystallisation can even create compressive strength. We can hypothesise that the observed cracks originated close to the interface with the brick, where salt had accumulated, and propagated towards the surface. Additionally, the salt present in the brick is progressively transported to the plaster layer, further contributing to intensifying the damage. The plasters did not show visible damage when the water absorption test was performed with the plaster surface in contact with water, possibly because the salt accumulated mostly close to the interface with the brick and was driven towards the brick exposed surface during the water absorption process.

Figure 4. Aspect of the plaster/brick salt-contaminated specimens after the water absorption by capillarity test with the brick surface in contact with water.
Fig. 5 shows the drying curves of mould mortar vs. plaster/brick specimens. Fig. 6 shows the drying curves of brick saturated with water (B/R) and salt solution (B/S), and salt-free and salt-contaminated L and LO plasters. The drying coefficients and drying indexes calculated from the drying curves is given in Tab. 3; the amount of salt efflorescences collected from the salt-contaminated materials at the end of the experiment is also given. Two drying stages can be identified in all evaporation curves [17]; in Stage I, also called constant-rate period, the moisture content decreases more or less linearly with time (saturated condition at the surface); in Stage II, the drying rate falls, which finds expression in the concave form of the curve. The curves in Fig. 5 show that the drying kinetics of L and LO mortars are very similar. Therefore, one could conclude that the addition of the hydrophobic admixture does not affect the drying rate in L mortar. However, when applying the same mortar as a plaster on brick, the drying rate is not affected for L, but LO plaster significantly reduces the drying rate and the global drying kinetics of the system. This phenomenon can be assigned to the fact that LO plaster creates a liquid transport resistance between the brick and the plaster. The salt-free brick (B/R) and the lime plaster/brick system (L/R) have very similar drying kinetics as the drying coefficients and drying indexes show. Plaster L/R dries slightly faster than B/R, as expressed by both the lower drying index and higher drying coefficient, indicating that lime plaster slightly enhanced the drying process. This phenomenon can be attributed to the fact that lime can increase the effective surface of evaporation during the Stage I of drying [22].

![Figure 5. Drying curves of mould mortars (M) and plaster/brick systems (R).](image)

![Figure 6. Drying curves of: a) salt-free (B/R) and salt-laden brick (B/S) and b) lime and lime with oil plaster cured on salt-free (L/R and LO/R) and salt-laden brick (L/S and LO/S).](image)

Drying is faster with water for all the materials, as expected. The evaporation rate in the presence of salt is lower because the salt depresses the RH_{eq} of the liquid, among other factors like the pore clogging effect due to precipitation of salt [23]. However, as Fig. 6 shows, the presence of salt influences more significantly the Stage II, as expressed by the higher drying index and analogous drying coefficient of the salt-contaminated materials in comparison with
the salt-free systems (Tab. 4). Plaster LO/S shows slightly slower drying coefficient and higher drying index than LO/R. The results suggest that the presence of salt does not significantly affect the drying kinetics of L plaster as it affects LO.

Table 4: Drying coefficient, drying index and amount of salt efflorescences exuded from the salt-contaminated materials after drying. The values are the average of 4 specimens.

<table>
<thead>
<tr>
<th></th>
<th>L/M</th>
<th>LO/M</th>
<th>B/R</th>
<th>B/S</th>
<th>L/R</th>
<th>L/S</th>
<th>LO/R</th>
<th>LO/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying coef. (kg·m⁻²·h⁻¹)</td>
<td>0.10 ±0.01</td>
<td>0.09 ±0.001</td>
<td>0.13 ±0.002</td>
<td>0.08 ±0.003</td>
<td>0.16 ±0.002</td>
<td>0.13 ±0.005</td>
<td>0.04 ±0.001</td>
<td>0.03 ±0.002</td>
</tr>
<tr>
<td>Drying Index</td>
<td>0.19 ±0.01</td>
<td>0.15 ±0.002</td>
<td>0.14 ±0.001</td>
<td>0.26 ±0.005</td>
<td>0.12 ±0.01</td>
<td>0.17 ±0.005</td>
<td>0.51 ±0.03</td>
<td>0.63 ±0.01</td>
</tr>
<tr>
<td>Salt efflor. (wt.%)</td>
<td>- ±4.9</td>
<td>- ±1.4</td>
<td>-</td>
<td>49.2</td>
<td>-</td>
<td>64.3</td>
<td>-</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Fig. 7 shows the aspect of the samples at the end of the drying experiment (20 days). The surface of L/S plaster became entirely covered by long whisker-like efflorescences after 96h. Plaster LO developed a powdery crust of small crystals confined to some areas close to the borders. The surface of the plaster looked darker around the efflorescences, indicating the presence of moisture assigned to the hygroscopicity of the salt. After removing the salt efflorescences at the end of the test, the surface of L plasters did not show visual alterations, whereas the LO specimens exhibited moisture stains where the salt efflorescences had developed (Fig. 7.b).

Figure 7. Aspect of the salt-contaminated brick/plaster systems at the end of the drying test: a) salt efflorescences formed on the surface, b) plasters’ surface after brushing the salt efflorescences.

The amount of salt efflorescences exuded from B/S corresponds to ca. 50 wt.% of the salt initially absorbed by the brick (Tab. 4). Regarding L/S, 60 wt.% of the salt precipitated as salt efflorescence. In contrast, in LO/S only ca. 6 wt.% of the salt effloresced. These results suggest that L plaster can be very effective in transporting salt to the surface, whereas LO blocks salt migration. Given that a significant part of the salt is removed from L/S plaster during the first hours of drying, the effect of pore clogging by salt can be considered negligible and explains why the drying rate is not significantly affected by the presence of salt. On the other hand, in the case of LO/S, the pore-clogging effect [23], especially at the interface between the plaster and the brick as shown in the OM images (Fig. 1), can have influenced the drying kinetics. The presence of salt efflorescences and its morphology can
also interfere with the drying behaviour of the materials [24]. Since the drying curves between L/R and L/S are very similar, we can assume that the porous layer of salt efflorescences formed in L/S had very little or no obstructive effect in the evaporation process.

The interface between different pore systems plays an important role in determining the location of salt crystallisation [9]. Petkovic et al [6] studied the drying of water and NaCl saturated plaster-substrate systems and concluded that if the pores of the plaster are smaller than those of the substrate, the salt is removed from the substrate and accumulates in the plaster. If the pores of the substrate are smaller than those of the plaster, some salt crystallises in the plaster layer, but a significant amount of salt remains in the substrate. Therefore, because L plaster has the main pore size volume lower than that of the brick, the plaster is effective in transporting the salt from the substrate to the surface. Regarding the PSD, we could infer the same about LO plaster. However, LO plaster pores are hydrophobic; hence, the capillary transport of salt solution from the substrate is hampered.

4. Conclusions

The study on the effect of the salt contamination of the brick in the properties of lime and lime with oil plasters gave important information regarding the hydric and hygric behaviour of the layered samples. The study has clearly established the important influence of the salt contamination of the substrate in the curing process of the plasters and, consequently, in their performance. Lime mortar works as a salt-transporting plaster whereas lime with oil functions as a salt-blocking plaster already during curing, and the salt accumulates preferentially at the interface between plaster and brick. The hydrophobicity of the lime with oil plaster was significantly reduced during curing by the salt-contaminated brick and the plaster developed cracks when moisture moved from the brick towards the exposed plaster surface. Thus, in real conditions, it is crucial to know the moisture sources and the nature and amount of salts present in the substrate before selecting a repair mortar. The salt contamination of the substrate is an aspect that should be accounted for the performance of mortars before considering its application in real conditions. Ongoing field observations in a masonry wall with high sulphate content rendered with the hydrophobic mortar have already confirmed the laboratory results; extensive cracking of the renders was observed after one month.

Acknowledgements

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References

SALT CONTAMINATED SANDSTONE UNDER ENVIRONMENTAL LOADING: RECRYSTALLIZATION PROCESS AND ITS CONSEQUENCES

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Abstract
Porous materials that contain salts can be permanently exposed to dissolution/deliquescence-drying cycles. Here we report that the mechanisms of salt precipitation are the key factors that determine the drying behaviour of salt contaminated porous materials and the physical weathering generated by salt precipitation. We present macroscopic and microscopic scale experiments, using magnetic resonance imaging, phase contrast microscopy, and X-ray tomography, assessing the impact of the recrystallization dynamics of NaCl and Na2SO4 on evaporation and damage observed in sandstone. When the same amount of water is used to dissolve the salt present in a stone, depending on whether this is done by a rapid saturation with liquid water or by a slow deliquescence using water vapor, different evaporation kinetics and salt weathering due to different crystallization pathways are observed.

1. Introduction

Artworks such as sculptures, historical monuments, frescos are subject to physical and chemical changes over time. A major problem in the conservation of especially historical architecture is their deterioration due to the action of salts. Most of the monuments are made of porous stones, and the pore network can contain both salts and water. These salts can be derived from external sources, for example from ground water or carried by the wind, or they can be naturally present in the stones or mortars used for construction. Subsequently, these entrapped salts can dissolve again in two different ways: by bringing it in contact with liquid water (dissolution) or by contact with water vapor (deliquescence). The latter is due to the hygroscopic properties of salts. The resulting salt solution is subsequently mobilized in the porous network and re-crystallizes when drying again.
The action of salts on water evaporation from porous media and their action on weathering stones has attracted a lot of attention over the past decade. These studies have revealed the impact of the pore size [1,2] and the relative humidity [3,4] on the type of crystallization. However, one important aspect that is still ill understood is the dynamics of the crystallization and recrystallization processes [5-9]. Depending on whether the salt re-precipitation occurs directly from a homogeneous salt solution or from pre-existing crystallites present in the solution, different growth rates and crystallization patterns can result. For example, the evaporation of homogeneous pockets of salt solutions in confined systems (i.e. entrapped liquid in the pore network) can lead to high supersaturations prior to crystallization [10]. On the other hand, new crystals precipitation from pre-existing crystals typically happens around the saturation concentration [11,12]. It is clear from the above that the crystallization dynamics in a porous medium depends on both thermodynamic and transport processes. In this paper we discuss to what extent the precise dynamics of recrystallization is important in evaporation and the damaging process.

2. Experimental procedure and results

We have performed a multiscale study on the behaviour of NaCl and Na2SO4 contaminated sandstones, subject to dissolution and deliquescence and followed by drying in controlled environmental conditions RH~ 50%, T=21°C. The type of sandstone used in this study is Mesne sandstone with a porosity 29% and pore diameter dp~ 30 μm determined by mercury intrusion porosimetry [13]. The mineral composition of the stone, obtained by XRD, consists of 90% Quartz and 10% of Kaolinite, a non-swelling clay mineral. Two salts were used in the study: (a) sodium chloride which has a cubic anhydrous structure at room temperature. Saturated sodium chloride solutions (26.4% wt or 6.1 molkg⁻¹) are prepared with NaCl (Sigma Aldrich grade). (b) Sodium sulfate which has anhydrous and hydrated (decahydrate and heptahydrate) crystalline structures [14,15]; At room temperature Mirabilite (the decahydrate form Na₂SO₄.10H₂O, with a solubility of 16.5 wt%, Cₛₐₜ = 1.4 molkg⁻¹ at 21°C). is known to be the thermodynamically stable state in contact with a saturated solution of sodium sulfate [14]. However, experimentally it has been shown that the spontaneous precipitation of thenardite (the anhydrous form with a solubility of 35 wt%, Cₛₐₜ = 3.8 molkg⁻¹ at 21°C) from homogeneous sodium sulfate solution can also occur at room temperature [5,16]. For the preparation of our salt solutions the solubility of mirabilite was taken as reference; That is saturate solutions were prepared at 21°C by dissolving thenardite (SigmaAldrich grade) slowly in ultrapure water up to a concentration of 16.5 wt% or 1.4 mol.kg⁻¹, i.e. supersaturation S=m/m₀=1) [5].

Sodium sulfate and sodium chloride contaminated sandstones were prepared by one cycle of impregnation and drying with saturated NaCl and Na₂SO₄ solutions. Most of the experiments were done using sample sizes of 20 x20 x 40 mm with volume to surface ratio of V/S= 4.4m. The sandstones samples were first saturated by spontaneous imbibition from the bottom in contact with either the NaCl or Na₂SO₄ solution. The complete uptake is achieved after 2 min; the amount of salt solution occupying the pore network is about MNaCl solution~4.95 g (M_water
~3.6g and M_{NaCl}~1.3 g) and M_{Na_2SO_4} solution=4.6g (with M_{water} ~3.8g and M_{Na_2SO_4}~0.8 g ). The local water saturation profiles, obtained by MRI, show a homogeneous distribution of liquid water into the sample prior to the drying step. The samples were subsequently dried on an automated balance with a precision of (+0.001 g) placed in the homemade controlled climatic chamber at T=21°C and RH~ 48%. The Relative Humidity in the climatic chamber is fixed by introducing water vapor at a controlled temperature into the chamber at laboratory environment. This is done by using water bath thermostat at T_1 ~9°C and flowing air through water at this temperature T_1. Once the air flow arrives in the chamber at the temperature T_2 ~21°C (laboratory environment), then the relative humidity of the chamber is fixed by the following equation:

\[ \text{RH} = \frac{p_w}{p_{ws}} \times 100\% \]  

where RH is the relative humidity (%), p_w the partial vapor pressure and p_{ws} the saturated vapor pressure at the laboratory temperature (2.64 kPa at 21°C). Since the flowing air is saturated with water vapor at 9°C, the partial vapor pressure is equal to the saturated vapor pressure at 9°C and the relative humidity will be settled at ~ 48%. In this way, our system permits to control a wide range of relative humidities very precisely.

Subsequently, we study the recrystallization in these salt-contaminated sandstones in two ways: by rewetting them with liquid water and in contact with water vapor (RH~100%). We consider that the saturation of the stone sample is complete when the amount of evaporated water M_{water} in the first cycle is again reached in the stone. After saturation, the drying kinetics (evaporation in 3D directions) are again followed in the same climatic chamber described above [8]. The dissolution/ deliquescence followed by drying (recrystallization) cycling are repeated up to 5 times for each sample.

Microscale experiments are used to investigate the recrystallization in the core of the stone and at the surface in more detail. These experiments are done using high resolution X-ray computed tomography (μ-CT), optical and Scanning Electron Microscopy (SEM) combined with Energy–Dispersive X-ray (EDX) [4,6-8].

Proton MRI techniques were used in order to follow the saturation profiles during the water uptake and drying of the salt contaminated stones. A Vertical Bruker Spectrometer with a field strength of 0.5T and 1d spin echo sequence were used in the study [8]. With MRI technique, only the mobile proton (i.e. water) is detected; the water in the hydrated crystals does not contribute to the measured proton density, because their NMR relaxation time becomes very short; they do of course contribute to the measured weight. Therefore the difference of sample saturation determined by the MRI technique and weight measurement allows us to calculate the amount of hydrated crystals that forms within the porous network during the drying in these cycling experiments.

The percentage of damage is assessed by gently removing the efflorescent salt, washing out the remaining salt, drying the stone and subsequently weighing the stone. The amount of damage is then given by the weight loss of the stone:

\[ \text{Damage} = \left( \frac{M_{\text{dry}}^{\text{initial}} - M_{\text{wash}}^{\text{final}}}{M_{\text{wash}}^{\text{initial}}} \right) \times 100\% \] 

\[ \text{(2)} \]
2.1 Recrystallization by Dissolution-drying experiments

The rewetting with pure water of the salt contaminated stones is done again by spontaneous imbibition as described above. The water impregnation is a rapid process (less than 2 min). With the water impregnation not all salt crystals at the surface will have time to dissolve and distribute again inside the porous network of the stone before the evaporation step. The distribution of salt ions in the liquid is consequently heterogeneous and the subsequent evaporation induces the precipitation of new crystals on top of the existing, incompletely dissolved ones. New crystals precipitation from pre-existing crystals is also known as secondary nucleation and typically happens around the saturation concentration (low supersaturation)[11].

Our results show that at RH~50% the drying kinetic is not affected by the recrystallization dynamics as is borne out by the observation that subsequent cycles do not lead to different drying rates. However, this has a deep impact on the crystallization dynamics and the crystalline structure that will precipitate. In particular, when the salt has different polymorphs with different solubilities.

In the case of NaCl, rewetting followed by drying leads to the formation of localised large salt crystals assemblies (cauliflower-like structures) at the surface as efflorescence (Fig.1). Because water was used for saturation, the observed precipitation of the new crystals at the surface thus implies the dissolution of crystals in other location within the sample and the transport of material to the place where the growth proceeds on the outer surface. Therefore rewetting with water followed by drying tends to extract the salt from the porous stone and favours the transfer of salt from one point to another. This leads to more localised spots of NaCl efflorescence as it can be seen in figure 1. In this case, hardly any damage is observed in the sample.

In the case of sodium sulfate Na2SO4, again more localised spots of efflorescence can also be noticed. Here, such crystal precipitation on the pre-existing ones favours the precipitation of mirabilite (the decahydrated form) because it has the lowest solubility. Microscale experiments in micro capillaries representative of one single pore show clearly that after a partial dissolution, the small thenardite crystallites that remain present in the solution act as nucleation sites for the rapid growth of a large amount of hydrated crystals, giving rise to structures that bear a similarity to a bunch of grapes (Fig.2)[7,8]. Moreover, our MRI saturation profiles, confirm such kinetics of growth of the hydrated phase: The evaporation rate obtained from the MRI saturation profiles (-0.31g.h⁻¹) is higher than the one obtained from weight measurement (-0.2g.h⁻¹). This difference can be related to the formation of hydrated crystals in the sample.
Figure 1. Salts contaminated stones (top images) are saturated with water and dried again (bottom images). Recrystallization in this way tends to extract the salt from the porous stone and favors more localised cauliflowers structures as efflorescence. X-ray μ-CT analysis of NaCl at the surface after dissolution recrystallization. The SEM images show the size increase of NaCl cauliflowers with dissolution-recrystallization.

The water molecules in the crystalline structure are not considered “mobile” and are not visible by MRI while these water molecules contribute to the weight measurements. In this way the amount of hydrated crystals (mirabilite) which are formed can be calculated. Our results show that after 5 h, 80% of the sulfate present in the stone is hydrated which thereafter leads to severe damage. We find that the amount of damage (granular disintegration) after one rewetting/drying cycle increases linearly with the initial concentration of salt in the stone and can be up to 8%[8].

Figure 2. left: Rewetting/drying: growth of hydrated crystals on the remaining thenardite microcrystallites in a microcapillary. Right: % of mirabilite formed in the sample. The latter is obtained from the difference in evaporation rate between the MRI measurements and the weight measurements during drying.
2.2 Recrystallization by deliquescence-drying experiments

In a humid environment (RH~100%), the weight of the sandstone without salt does not change as it contains very small amount of Kaolinite which is a non-swelling type. On the contrary, in the present of salts in the stone, the water uptake is found to depend strongly on the quantity of salt present (the solubility of each salt) and the equilibrium relative humidity above the salt (RH eq (NaCl)=75%, RH eq (Na2SO4)=93%) (figure 3). Due to their hygroscopic property, salt crystals deliquesce slowly and form a very homogeneous saturated salt solution which gradually invades the porous network of the stone. In this way, the dissolved salt is transported to the interior of the stone. We consider the sample saturated once the amount of evaporated water in the first cycle is introduced to the sample in order to form the saturated salt solution.

The subsequent drying of the saturated sample will consequently result to the spontaneous nucleation and growth of crystals from a homogeneous salt solution. This is known in the crystallization field as primary nucleation and high supersaturation can be achieved prior to salt recrystallization[10,11].

Our results for sodium chloride contaminated stones show surprisingly that the formation of large cauliflowers of crystals becomes almost completely absent in this second drying cycle after deliquescence. On the contrary, microscale analysis reveals the precipitation of large cubic crystals (Fig.3); their formation is usual for recrystallization from homogenous solution because at each cycle impurities are expelled [4].

![Figure 3. left: The MRI saturation profiles of the water uptake of sodium sulfate contaminated sandstone (20x20x40mm) due to the deliquescence of the entrapped sodium sulfate crystals when exposed to a humid environment of RH~100%. The complete homogeneous saturation is achieved after 70 days. Right: the case of NaCl contaminated in a half size sample (20.5x20x20 mm).](image)

The increase of salt concentration in the solution before recrystallization reduces the wetting properties of the solution; this leads to an increase of the surface tension and contact angle of the salt solution, measured experimentally, as \( \gamma_v = 13.826 (S) + 71.38 \) and \( \theta_v = 20.11(S) + 30.41 \) with \( S = m/m_0 \) where \( m_0 \) represents the saturation concentration (6.1 mol.kg\(^{-1}\)) and \( m \) the NaCl concentration in the solution [4]. The reduction of the wettability properties could favor the...
retraction of the solution into the porous network and subsequently the crystallization in the subsurface as it is clearly visible from X-ray microtomography images.

![Figure 4. Deliquescence drying cycles. SEM images of the core of the sample (horizontal cut) showing salt crystals in the subsurface (subflorescence). SEM pictures of cubic crystals between the grains at the subsurface after 3 cycles of deliquescence/drying.](image)

In the case of sodium sulfate, the drying of saturated sample is followed with MRI techniques. A very homogeneous desaturation of the sample during evaporation is occurred. On the contrary to dissolution-recrystallization, no discrepancy is observed on the evaporation rate determined by the two methods MRI and weight measurement (Fig.4). In both cases the evaporation rate is of the order of -0.17g.h\(^{-1}\). This result suggests that after complete deliquescence and with the second cycle of drying, only anhydrous crystals (thenardite) recrystallize within the porous network; the water molecules do not contribute in the crystalline structure and consequently remains visible in MRI, as mobile water.

Microscale experiments in single square microcapillaries representative of a single pore in the porous network confirm well that with increasing the number of cycles of deliquescence/drying, there is a retraction of the salt solution in the microcapillary due to the increase of concentration and the change in the wetting properties of the salt solution (fig. 5).

For sodium chloride solution, the salt microcrystals which have precipitated as efflorescence at the exit of the tube deliquesce and form a saturated salt solution; The latter invades the tube due to capillarity. With the evaporation, the salt solution retracts in the microcapillary and reaches supersaturation around 1.8 at the onset of crystallization. The precipitation leads to the formation of mostly one cubic crystal growing in size with further evaporation[4].

For sodium sulfate, the salt solution reaches also high concentration (S=3.05 with respect to the solubility of mirabilite, S=1.15 with respect to the solubility of thenardite) prior to recrystallization. Surprisingly, the recrystallization from the homogeneous solution leads to the direct growth of thenardite based on the phase diagram of sodium sulfate [13]: Thenardite is the crystalline phase with the higher solubility. The reason why hydrated crystals do not nucleate in the solution with such a high supersaturation with respect to the formation of this phase is still unclear and under investigation.

Moreover, the amount of damage quantified in the samples even after several cycles (up to 5 in our experiments) is lower than 0.5%, when only thenardite precipitates during evaporation
For sodium chloride, deliquescence/drying cycling leads to 5% damage in the form of granular disintegration in good agreement with previous work showing that NaCl under humidity cycling can lead to damage [16].

Figure 5. (a-c) deliquescence of NaCl crystals as efflorescence outside of capillary and recrystallization of one cubic crystal inside of the microcapillary at S=1.8. (d-f) deliquescence of Na$_2$SO$_4$ crystals in a microcapillary and recrystallization of thenardite at S=3.05 (with respect to the solubility of mirabilite). The size of the microcapillary is 100 $\mu$m.

Figure 6. The important role of recrystallization dynamics on Stone Damage. While humidity cycling is harmful for NaCl contaminated stone (left image), rewetting-drying leads to severe damage in Na$_2$SO$_4$ contaminated stones (right image).

3. Conclusion

We have elucidated the major role played by different salt crystallization pathways on the behavior of salt-containing sandstones subjected to several wetting-drying cycles. The kinetics of crystal growth, notably whether the nucleation is primary or secondary strongly influences the drying behavior, the precipitation of different polymorphs and the weathering of the stone.

For sodium sulfate, with both hydrated and anhydrous phases, the results show that hardly any damage occurs for deliquescence/crystallization cycles which induce the precipitation of thenardite (anhydrous polymorph) whereas dissolution/crystallisation cycles can lead to granular disintegration (Fig. 6) due to the precipitation of mirabilite crystals (hydrated polymorph) on incompletely dissolved anhydrous sodium sulfate.
On the contrary, the rewetting of the salt contaminated stones with liquid water progressively extracts the salt from the porous medium forming localized spots of efflorescence. For NaCl this leads to the formation of a few large microcrystallites assemblies at the surface without damage. In contact with water vapor, the deliquescence of the salt leads to a complete dissolution and the transfer of the saturated salt solution into the porous network. The evaporation of the homogeneous salt solution that forms, induces the recrystallization of large cubic NaCl crystals which progress towards the interior of the stone core after several cycles (subflorescence) which leads to the granular desintegration.

These results show how the kinetics pathway of recrystallization of NaCl and Na2SO4 influences the way these salts cause damage under different environmental conditions. It has often been assumed that the crystals forming within the stone (subflorescence) or at its surface (efflorescence) is a property of the specific salt that is present; Our results show that for the same salt, both phenomena can be observed depending on the environmental conditions which induce the recrystallization. This opens the way to a better understanding of salt damage by these two important salts, but also suggests how to best desalinate contaminated stones depending on the nature of the salt.

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References

WICK ACTION IN POROUS BUILDING MATERIALS AS STUDIED BY NMR

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Abstract

Salts crystallization is one of the main degradation mechanisms of historical objects like masonry. In this study we looked at a special case for crystallization, i.e., wick action. This is a steady state situation where one end of an object is continuously absorbing a salt solution, whereas at the other side there is a continuous drying. As a result there will be a continuous flux of ions to the surface resulting in a crystallization at the drying surface. In this study we looked at wick action for both NaCl and Na2SO4 using a biomicritic limestone from Sardinia where it is found in many cultural heritage objects. To measure both moisture and salt simultaneously, we have used a specially designed Nuclear Magnetic Resonance (NMR) instrument.

1. Introduction

Salt crystallization is one of the main degradation mechanisms of historical heritage objects, such as masonry. Moisture penetration can bring dissolved salt along with it into a porous material. The salt can accumulate and crystallize in the pores and can as a result produce cracks due to crystallization pressure. To get a better insight into the salt transport mechanism we examined the situation when a porous material is in contact with salt solution on one side and at the same time is exposed to drying conditions on the opposite side. This situation is often encountered in cultural heritage where for example a masonry wall is in contact with groundwater, or open water as is often seen in the case of the historic city of Venice. This continuous transport of a salt solution, combined with drying, is referred to as wick action (see also Fig 1). During wick action salt ions will penetrate by two main mechanisms, advection and diffusion. Advection is the process of ions moving with the moisture flow in the void space, whereas diffusion is dependent on the concentration gradient, i.e., diffusion
tries to level off any concentration gradient. The net ion flux will be a competition of these two processes. Due to the continuous flow of salt ions towards the drying face there will be a continuous accumulation and as soon as the maximum solubility limit has been reached, there will be crystallization, either inside the materials (subflorescence) or outside (efflorescence). In this study we have focused on equilibrium wick action, when the conditions of exposed faces to the solution and air are stationary and the porous medium stays water saturated throughout the process, i.e., without forming a drying front inside of the material [1,2]. Hence we do not take into account the changing of the boundary conditions as would be seen in situ, i.e., due to changing weather conditions. In this study we have used Nuclear Magnetic Resonance (NMR) to measure both moisture and ions nondestructively and quasi-simultaneously during wick action experiments. These experimental results have been compared to a numerical solution of the advection-diffusion equation (ADE).

Figure 1. A schematic representation of wick action in porous material. There will be an advection of ions to the top of the sample, whereas at the same time diffusion wants to level off any accumulation.

2. Material and methods

For this study we have looked at a biomicritic limestone from Sardinia which is found in many cultural heritage objects there. It has a porosity of 0.34, pore size with the maximum of the distribution at 1.6 μm and has only very minor magnetic impurities. For the experiments we used cylindrical samples with a diameter of 20 mm and length of 86 mm, which were drilled out of a larger block. After rinsing the sample in clean water, the sample was dried at 40 °C until constant weight. The experiments were started with samples, which were vacuum saturated with distilled water. To perform 1D experiments the specimens were isolated on the sides with Teflon tape. The experimental setup is given in Figure 2.
Figure 2. A schematic representation of wick action setup as used in the NMR. Using 2 pumps the concentration is maintained constant at the bottom of the sample. A reference solution is incorporated in the setup in order to check for long term stability.

The sample holder is a Teflon cylinder with solution reservoir at the bottom and air flow inlet and outlet at the top to provide drying at the top of the sample. The bottom of the sample is in contact with a salt solution. To maintain a constant concentration, this is circulated with the help of 2 pumps with a large reservoir. To cause drying, the top of the sample is exposed to a constant air flow of 10 L/m at 0% relative humidity. An evaporation shield has been added to separate the drying and absorption part, i.e., to limit the influence of the drying on the bath concentration. During the experiment the mass of the bath is measured continuously. A stepper motor was used to move the sample holder vertically inside the NMR as to be able to measure the moisture and ion profiles. Signal can be obtained only from free ions and not any sodium nuclei incorporated in crystals can be detected. The spatial resolution in vertical direction for hydrogen nuclei is 1.27 mm and for the sodium 5.5 mm.

The salts used in this study are sodium chloride (NaCl) and sodium sulfate (Na2SO4). These salts are the most common in salt crystallization decay of heritage objects. Sodium chloride has one stable phase and the solution saturates at 6.1 Mol/kg. Sodium sulfate solubility is strongly temperature dependent. Sodium sulfate has different polymorphous forms [3,4]. Under room conditions of 18 °C, as used in our experiment, two phases can be formed: the hydrated phase, i.e., mirabilite (Na2SO4.10H2O) and the metastable phase (Na2SO4.7H2O) [5].
3. Experimental results

The first experiment was performed with samples saturated with 2M/kg sodium chloride solution. The NMR signal was collected from cross-sections of the sample in 1.27 mm steps along the axis of the cylindrical sample. Figure 3 shows the measured moisture and sodium ions profiles over 8 days. The profiles were measured every 2 hours. The profiles are for 55mm of the total length, because the 31mm of the sample from the bottom was placed inside the solution in the reservoir, and the signal collected from this part is not only from the ions in the pores of material, but also from the solution in the reservoir. Bottom of the sample is in contact with the reservoir and as can be seen during the time of this experiment the concentration remains almost constant at position $x = 0$ which is just above the bottom. As soon as the drying has started the concentration at the top, represented at $x=55$ mm, starts to increase slowly. About 2 days after the start, the concentration reaches the maximum of 6.1 Mol/kg and any additional advection will result in crystallization within the material. From this moment on, the concentration remains constant at the top and the maximum concentration in the sodium profiles which defines crystallization front is seen to be moving inward. At the same time it seems that the crystallization does not have a large influence on the moisture transport. After 8 days of NaCl wick action, when the sample was removed from the NMR, a very thin layer of efflorescence was seen on top of the sample. To get some more information on the crystallization process, we have plotted the displacement of maximum concentration as a function of time in figure 4. It represents the crystallization front movement. As can be seen, it seems that in first order approximation the speed is almost constant.
The same experiment was repeated with a 0.5 Mol/kg sodium sulfate solution. The results are given in Figure 5.

Figure 4. Position of crystallization front as a function of the time for a wick action experiment with NaCl (see fig 3) and Na_2SO_4 (see fig 5).

Similar results can be seen as for NaCl. In this case the concentration measured at the top seems to indicate the metastable heptahydrate is being formed. As can be seen from the moisture profiles also in this case the crystallization does not seem to have a large effect on the moisture transport. In contrast to NaCl, after 12 days wick action, there was still not any efflorescence observed for Na_2SO_4. To check whether indeed the metastable heptahydrate is being formed, at the end of the experiment the top of the sample was brought into contact with a mirabilite crystal. The dashed lines in Figure 5. indicate the profiles after contact with mirabilite. As can be seen the concentration decreased and the space occupied by the crystals, as determined from the moisture profiles, increased. This is a clear indication of the fast transformation of heptahydrate into mirabilite. The position of the crystallization front is also plotted in figure 4. As can be seen also in this case an almost constant speed is observed. Although the speed is much less than was seen for NaCl.
Figure 5. The measured (a) hydrogen and (b) sodium profiles for a wick action experiment with Na₂SO₄ for total of 12 days. The sample was initially water saturated. The dashed lines in both plots determine the profiles after placing mirabilite on top of the sample.

4. Numerical model

To get a better understanding of the processes taking place during wick action we have done various numerical simulations. During wick action the ion transport can be described by an advection-diffusion equation (ADE) as given by:

\[
\rho \varphi \frac{\partial}{\partial t} C(x,t) = \frac{\partial}{\partial x} \left[ \rho \varphi D \frac{\partial}{\partial x} C(x,t) - \rho \varphi v C(x,t) \right] + S(x,t)
\]

(1)

where \( \rho \) and \( v \) are respectively bulk density and fluid velocity, \( \varphi \) is porosity and \( C(x,t) \) is ion concentration. \( D \) [\( m^2/s \)] is the effective diffusion coefficient of the ions in a porous material. \( S(x,t) \) represents a sink term, which can be both crystallization but also dissolution. For wick action the initial and boundary conditions are given by:

\[
C(x,0) = C_0
\]

(2)

\[
\frac{\partial}{\partial x} C = 0 \quad \text{when } x = 0, \ t > 0
\]

(3)

\[
D \frac{\partial}{\partial x} C(x,t) - v C(x,t) = 0 \quad \text{when } x = L, \ t > 0
\]

(4)

When \( C_0 \) is the concentration at the reservoir and \( L \) is the length of the porous column.

A numerical model has been developed by solving ADE with MATLAB pdex. As a first step the equation was solved without taking into account any sink term due to crystallization.
this case the model is expected to explain sodium penetration and the concentration build up at the drying face before it reaches the solubility limit. Figure 6 shows the model output before and after applying the 5 mm resolution of the NMR on the simulated profiles. To compare the simulation with the experimental profiles, the resolution ($\delta x$) of measurement is taken into account by changing the simulation profiles at $x=L$ and replacing it by an exponential fit from $L-\delta x/2$ to $L+\delta x/2$. The parameters in this simulation were chosen in accordance with the NaCl experiment, i.e., the velocity of the fluid used was calculated from the mass change of the bath. As can be seen this simulation captures well the initial increase of the concentration near the surface.

Figure 6. The result of a simulation of the initial wick action for NaCl. for a total of 50 hours. The dashed lines are simulation results without applying the resolution and the full lines are after applying the resolution.

5. Conclusions

The experimental data for both sodium sulfate and sodium chloride shows the overall similarity of sodium ion penetration into limestone in terms of ion accumulation and crystallization front movement in the material during wick action. The numerical model shows the early ion accumulation on the drying face; however, to predict this behavior for longer time it is necessary to take precipitation and dissolution into account.

References


POULTICING VS ELECTROPHORESIS DESALINATION OF HISTORIC MASONRY, THE CASE OF THE MILL AT HOKSEM

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Abstract

Salts in historical masonry are a known destructive force and despite extensive research the results of desalination procedures remain unclear. A common used method for salt extraction is the use of poultice materials, while a more experimental technique is electrophoresis. In-situ the processes of both methods remain empiric and the results are more or less random. For the success of a salt extraction it has become clear that it is crucial to evaluate certain parameters before taking action. This paper deals with the state of the art of desalination of historic masonry by means of poulticing and electrophoresis, based on results of a case study. Both methods have been applied on a historical masonry of a barn in the old mill house in Hoksem-Hoegaarden, Belgium. The results of poulticing indicate that the efficiency is rather limited, especially for the brick and in the depth of the masonry, and that salts are often redistributed in the masonry. While electrophoresis tests show more positive results in terms of desalination in the depth of the brick and mortar, several important questions related to the method for evaluating the salt extraction effect as well as to the formation of potential dangerous compounds remain unanswered.

1. Introduction

It is generally known that when a salt concentration becomes high enough it can become destructive to porous building materials used in historical masonry. Regardless of the presence of water as a liquid or vapour, repeated cycles of dissolution, hydration and crystallization of salts can cause damage. Hence, the removal of salts contributes to a sustainable preservation strategy. Salt extraction of masonry by poulticing is often the only readily available option, however mostly carried out on the basis of general assumptions and without control of the efficiency nor of the effect deeper in the masonry \cite{1, 2}; in no way a long term effect is approached. This paper describes the results of two different types of salt extraction techniques
carried out on historical masonry of a barn belonging to a historic mill house in Hoksem-Hoegaarden, Belgium. The in-situ tests consist of using a poultice applied according to the principle of advection as described in [3-6] and an alternative yet experimental method to extract salts by electrophoresis [7-10].

The results are compared and evaluated to further the understanding of the extraction processes and address critically the method of evaluating in-situ the effectiveness of poulticing versus electrophoresis, more specifically in terms of the salt content in the poultice or buffer material and in the depth of the masonry before and after the desalinization treatment. The effect of salt removal is controlled by ion chromatography of the aqueous extract of samples lifted in the mortar and brick at different depths. The tested zones are highly contaminated with mainly potassium chloride, sodium carbonate and nitrates, of which the mortar and brick show severe salt damage in the form of sanding. The choice of this onsite application was based on its conservation state, revealing the need for a durable intervention.

2. Methodology and materials

2.1 General sampling and salt analysis

Drilled samples are taken from mortar and brick at several locations and at different depths (0-2, 2-5 and 5-10 cm) before and after each desalination treatment, as well as from the poultice and buffer materials. From each sample, approximately 1 g, the actual moisture content is determined by comparing the initial weight to the weight reached after drying at 60°C. The hygroscopic moisture content is determined by conditioning the dried sample at 95% RH until constant weight. The hygroscopic moisture content is calculated from the increase in weight. Deionized water (100 ml) is added to the samples. The solution is mixed to dissolve ions followed by filtration. From the extract, sodium (Na+), potassium (K+), calcium (Ca2+) and magnesium (Mg2+) cations and chloride (Cl−), nitrate (NO3−) and sulphate (SO42−) anions are quantitatively (ppm) determined with Ion Chromatography (IC, Metrohm). From the excess of cations (excluding Ca2+ ions associated to SO42−) the amount of soluble carbonate (CO32−) is calculated.

The salt contents presented in this paper contain the sum of detected ions excluding equimolar amounts of Ca2+ and SO42−, and including the theoretical amount of soluble CO32−; the latter is not included for the buffer materials used for electrophoresis. Unfortunately, for the electrophoresis buffer a fault margin of ±15% cannot be overcome due to the excess of anions that might be associated with other compounds. Gypsum considered less destructive was not addressed in the evaluation method as its inclusion would overshadow the salt extraction effect. Salt contents are expressed in kg.m−2, calculated based on the density of the material, at different cumulative depths to 10 cm and intermediate depths as described earlier. For the masonry the salt content is calculated considering the specific density of the dry powdered mortar (2518,60 kg.m−3) and brick (2524,95 kg.m−3). For electrophoresis the density of the buffer material of dry calcite (2710,00 kg.m−3) is considered while for poulticing that of the dry poultice material (1080,40 kg.m−3). The average salt content expressed in kg.m−2 in the masonry is calculated considering the specific surface area of both mortar and brick (15x4 cm² for brick and 1,5 cm of mortar in between).
2.2 Poulticing procedure
The onsite application concerns one area of 3 m² of brick masonry with a thickness of about 40 cm of an interior façade. The poultice material is an experimental poultice produced by Rewah and contains recycled cellulose fibres, Kaolin Speswhite clay, calibrated sand (0.5-1 mm) (1-2-1 ratio by weight) and a water content of 0.8-1 to 1-1 (weight water - weight dry poultice). The dry poultice has a total porosity of approximately 50%, determined by mercury intrusion. The experimental procedure of one poultice application consists of: 1) selecting a zone based on the results of the salt content of samples lifted at different depths from the salt deteriorated mortar and brick; 2) pre-wetting (by spraying) the surface of the substrate with 2 l.m⁻² pure water; 3) application of the poultice with a thickness of approximately 1 cm (figure 1); 4) removal of the poultice after 6 days of drying and 5) controlling the salt content of drilled samples of brick and mortar at three different locations, one in each m² (shown in figure 1), as well as of the poultice material. The procedure is repeated entirely with the difference of pre-wetting the surface with 0.5 l.m⁻² and removal of the poultice after 10 days.

Figure 1. The poultice applied on the masonry in-situ (3 m²), the sampled locations are shown with circles.

2.3 Electrophoresis procedure
Four separate test zones (60x60 cm²) on the same interior side of the façade of the barn are selected; half of them are pre-wetted with 2 l.m⁻² and the other half with 15 l.m⁻² of demineralized water. The pre-wetting is carried out on enlarged zones of at least 100x100 cm². During pre-wetting, the test setup is prepared. For that, the buffer material consisting of a mixture of calcite and recycled cellulose (5-1 ratio by weight) and a water content of 1.5-1 (weight water over weight dry material) is applied in a thickness of approximately 1 cm on the wooden board onto which the electrode plates (15x15 cm²) are positioned at a distance of 15 and 30 cm (figure 2). Immediately after, the test zones are subjected to a current of 20 volt through the masonry over a period of 14 days during which ions migrate to the opposite charged electrode. In case of sodium salts, sodium hydroxide is formed at the cathode or negatively charged electrode [11], hereby creating an alkaline environment that is considered not
damaging for the masonry. At the positively charged anode water is transformed into oxygen and hydrogen ions. The latter combine with chlorides to form hydrochloric acid. Sulphates present in the solution will similarly combine with the hydrogen ions and form sulphuric acid. It is evident that such an acidic environment can chemically attack the calcium carbonate of building materials and cause damage. The buffer material is used to accumulate ions and protects the building material from acidic attack and hence damage [12]. The electrophoresis effect of the four test areas is evaluated by comparing the salt content after the salt extraction process with the initial value according to the test procedure described earlier.

![Figure 2. Example of two test zones for electrophoresis. The buffer material is applied between the masonry and the wooden board onto which the graphite electrode plates are fixed. Through holes in the boards the electrodes are connected to the electrical circuit, which is logged throughout the process.](image)

3. Results of the desalination by poulticing

The salt content, averaged over the three measuring points, after each poultice application reduces significantly in the mortar up to a depth of 10 cm (figure 3), the maximum depth where samples were lifted for analysis, while that of the brick reduces slightly up to 5 cm depth and then increases deeper in the wall (figure 3, circle). When comparing the amount of salts detected in the poultice after the first and second application with the total salt content in the first 2 cm of the masonry before treatment (brick and mortar) an efficiency of respectively 35% and 29% is achieved, indicating that per application about one third of the reduced salt content within the first 2 cm is found within the poultice. The mortar contributes to a higher part of the salt reduction. However, the poultice efficiency reduces when the cumulative salt reduction is considered up to greater depths within the masonry. The effect is already noticeable for the first
application, but increases significantly when evaluating the second one, ending with a negligible poultice efficiency of 5% in case a depth of 10 cm is considered, although the salt reduction in the masonry is 20% at this point (figure 4).

Figure 3. Salt content (kg.m$^{-2}$) averaged over 3 tested areas in the poultice and the cumulative amount with depth in the brick or mortar before and after two poulticing procedures. The circle indicates the increase of the salt content in the brick after treatment deeper in the wall.

Figure 4. Average reduction (%) of the 3 tested areas, of the cumulative salt content in the depth of the masonry (brick and mortar) after each poulticing procedures.

4. Results of the desalination by electrophoresis

The influence of the distance between the electrodes (15 or 30 cm) on the electrophoresis effect was negligible. A general lower efficiency is noticed in case of pre-wetting with 2 l.m$^{-2}$ compared to 15 l.m$^{-2}$ [8]. It should be mentioned that in case high amounts of water are used during pre-wetting, one is confronted with the migration of salts deeper in the masonry. The results expressed as kg.m$^{-2}$ (figure 5) up to a depth of 10 cm reveal an average efficiency of 58% in the brick for the first two centimeters that decreases slightly to 40% to a depth of 10 cm, while for the mortar the salt reduction remains rather constant from 53% in the first 2 cm to 58% to a depth of 10 cm. A control of the electrophoresis was carried out by measuring the ion content of the buffer material lifted at the positive and the negative electrode (figure 5). As
expected, anions are mainly detected on the positive electrode (“anode buffer”) while cations on the negatively charged one (“cathode buffer”). In figure 6 the results are averaged for brick and mortar and for the four tested areas reaching 52% of salt reduction to a depth of 10 cm.

Figure 5. Average salt content (kg.m⁻²) of 4 test areas in the buffer material (after electrophoresis) and the cumulative content in the depth of the brick or mortar before and after electrophoresis (20 V, 14 days).

Figure 6. Average reduction (%) of the 4 tested areas, of the cumulative salt content in the depth of the masonry (brick and mortar) after electrophoresis.

5. Poulticing vs electrophoresis

To allow accurate interpretation of the results of both desalination methods, the salt content at intermediate depths before and after treatment are compared to the ones detected in the poultice and buffer materials (figure 7). After desalination by poulticing, the amount of salts deposited in the poultices is rather deceiving as the efficiency seems high when compared to the detected reduction in the first 2 cm of the masonry. However, it is clear from the balance that the salt content in the poultice deviates significantly from the reduction in the masonry to a depth of 10 cm. This deviation is most likely explained by the migration of salts deeper into the masonry after pre-wetting, leading to a negligible efficiency of just 5% to a depth of 10 cm. As no
samples were lifted beyond a depth of 10 cm, a certain amount of salts probably disappeared out of sight as they migrated deeper within the wall.

Figure 7. The sum of salts (kg.m\(^{-2}\)) in the 1\(^{st}\) and 2\(^{nd}\) poultices and in the anode (+) and cathode (-) buffers compared to the total salt reduction in the masonry derived from the average results after poulticing (3 tested areas) and electrophoresis (4 tested areas) shown in intermediate depths of the masonry (brick and mortar). The efficiency (%) of the desalination is related to the initial salt content in the masonry.

After electrophoresis the amount of ions detected in the buffer material at the anode and cathode corresponds well with the reduction in the masonry, that is, to a depth of 10 cm. The question remains how to quantitatively evaluate the effect of the electrophoresis more accurately, as it involves an electrokinetic phenomenon in which parts of the salts evaporate during the process like chlorides in the form of chlorine gas on one hand and in which other charged compounds can interfere on the other hand. The latter could be the case for gypsum and other mortar compounds for which the solubility is triggered by the continuous migration process typical for electrophoresis. This could explain the high calcium content detected in the buffer material at the anode. However, the amount of sulfate is too low at the cathode to explain such an effect. A plausible explanation could be the decomposition of the calcite buffer material in the acidic environment at the positive pole. This raises the question of possible back migration of calcium and other dissolved ions to the masonry. Another uncertainty is related to sodium ions that might exchange and form other potential dangerous compounds, in the form of carbonates and sulfates. Although it remains unclear what is left after the electrophoresis process the efficiency seems rather positive, reaching 52% to a depth of 10 cm.
6. Conclusion

Desalination procedures by poulticing and electrophoresis were carried out on historical masonry to assess the desalination processes in practice. The principle for evaluating the efficiency of the two desalination methods was similar by comparing the total salt content excluding equimolar amounts of calcium and sulphate ions and including the theoretical amount of dissolved carbonate ions, before and after treatment. For both methods a higher efficiency was reached in the mortar to a depth of at least 10 cm, while for the brick the efficiency was clearly lower and rapidly decreased with depth, the latter mainly for poulticing. It should be mentioned that in case high amounts of water are used during pre-wetting one is confronted with the migration of salts deeper in the masonry, which could explain the different results obtained for the salt reduction in the depth of the masonry compared to the salt content detected in the poultices.

It was shown that after pre-wetting the masonry with 2 l.m⁻² and the application of a poultice based on the principle of advection, the poultice was able to extract up to 35% of the initial salt content from the first two centimeters of the masonry, after 6 days of drying. However, the poultice efficiency decreases when the cumulative salt content is considered at greater depths in the masonry, where salts are likely redistributed to lesser salt contaminated areas or deeper into the masonry. The efficiency of poulticing can be considered low and becomes rather trivial, especially considering the brick. Furthermore, an average efficiency for the masonry of merely 5% is achieved to a depth of 10 cm. This proves the need to evaluate the salt extraction results at further depths in the different materials. In literature however, results are mainly limited to a depth of the first 2 to 5 cm and are not representative for the poultice extraction process and hence not necessarily compatible if one opts for a durable strategy.

After 14 days of electrophoresis at 20 V the reduction of the salt content to a depth of at least 10 cm in masonry reaches 52%. The salt content of the brick is reduced with 58% in the first two centimeters and 40% to a depth of 10 cm, while for the mortar the salt reduction remains rather constant with 58%. A significant excess of ions detected in the positively charged and acidic environment of the buffer material (anode) can partly be explained by an amount of dissolved calcium carbonate from the buffer material itself.

Both poulticing and electrophoresis have advantages and disadvantages for the extraction of salts from historic masonry. With poulticing producing relatively limited and superficial results, electrophoresis has a higher success rate concerning desalinating further in the depth of the different materials of masonry. However, in case of electrophoresis, lots of questions remain on how to evaluate the salt reduction effect, surely if parts of the salts remain in the porous solution and others disappear from the process. Do salt profiles, as found in literature, provide concise results? Another point is related to the decomposition of less soluble compounds, in the masonry and in the buffer material, for which the solubility might be stimulated during the electrophoresis process. Finally, more research is necessary to understand possible back migration of calcium and other dissolved ions to the masonry and the crystallization of the ion mixture including carbonates and sulfates left in the masonry after electrophoresis, if one wants to achieve a safe restoration intervention.
References


ASSESSMENT OF FLOOD AND WIND DRIVEN RAIN IMPACT ON MECHANICAL PROPERTIES OF HISTORIC BRICK MASONRY

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Abstract

As a result of increased rainfall and flooding the building fabric of historic structures in exposed areas are likely to be subject to higher and more sustained moisture content levels, along with experiencing an increased frequency and severity of wetting and drying cycles. This study aims to evaluate the impact of such cyclic wetting and drying on the mechanical behaviour of historic brick masonry. The reported results are obtained from a series of weathering and mechanical tests carried out on clay bricks and masonry specimens. The weathering test regime derives from analysis of observed weather data, combined with review of similar existing test protocols. Similarly, a modified mechanical test procedure is applied to simulate fatigue observed in the field. The results indicate that exposure to the weathering tests results in a reduction of masonry shear strength. This is discussed within the context of wider work carried out at a case study location, and highlights the value of designing a weathering regime that can more closely replicate the in-situ weathering processes. In this way the data collected in this experimental programme is shown to be suitable for use in contextual analysis of individual historic masonry case studies, with respect to climate change and the associated alteration of wetting regimes.

1. Introduction

Observations of changing trends in precipitation conditions are being regularly reported by the IPCC, with variance in precipitation conditions occurring at all geographical scales [1]. While some localised uncertainty does exist, one region of the globe has consistently exhibited a trend for increasing rainfall accumulations. Since the mid-20th cc. Europe has exhibited a consistently increasing trend in precipitation averages, contributed to by both seasonal conditions and extreme events [2]. Countries such as Norway and Poland have been shown to exhibit increases of up to 20% in daily precipitation totals [3,4]. Within the UK, total precipitation has been observed to increase between 10 and 50% in the second half of the 20th century [5]. In the future
the “contrast in precipitation between (…) wet and dry seasons will increase”, along with
projected further increases in overall precipitation levels of up to 30%. Extreme rainfall events
are already increasing in number [6] and projections indicate this trend will continue [7], which
only contributes to an increased risk of flood occurrence. Quantitative data that informs on the
mechanical resilience of masonry to these climate-induced moisture ingress processes is scarce,
with only a limited number of numerical approaches having been published [8, 9]. Similarly,
mechanical analysis of historic masonry in relation to these hazards is rarely studied, with any
work that has focussed upon flood and wind driven rain impact on historic fabric assessing
material decay through moisture ingress [10], salt movement [11] or drying regimes [12].

This study directly addresses this issue through the design and implementation of a series of
tests intended to generate empirical data informing on the relationship between weathering
conditions and mechanical response of historic masonry. The following section details the
design of the new weathering test sequence and apparatus, in conjunction with a review of
previous work. The remainder of the paper then sets out the detail of the test specimens used
within this experimental programme, followed by the presentation of test results. Discussion of
the findings focusses upon the value of the experimental data collected with regards informing
upon the future protection and continued resilience of buildings on site, including their
comparative use alongside monitoring data. The work was carried out as part of the Parnassus
project (2010-2014, see www.ucl.ac.uk/Parnassus), which brought together laboratory, in-situ
and numerical modelling investigations. Tewkesbury in Gloucestershire, England was one of
the case study areas and is the main focus of this paper. Tewkesbury is an early medieval town
located at the confluence of the River Avon and River Severn, and was chosen for its exposure
extreme precipitation and to floods, with the latest events in July 2007 and May 2012 causing
widespread damage. A 2001 study by Reynard et al. [13] has found that by 2050 the estimated
increase in rainfall could cause an increase in flow for the River Severn in the range of 20%,
significantly impacting on return periods of high flow events such as those leading to flooding
of the site. These conclusions are in broad agreement with the findings of later work by Smith
et al. (2014) [14], demonstrating that Tewkesbury constitutes a good location to study the
impact of flood and rain on the historic built environment.

2. Weathering regime design

The design of the weathering regime draws from various sources including observed climate
data at the test site, contextual trends sourced from historic met office observations and long
term conditions typical to the study area. The aim was to produce a set of test conditions that
were robustly linked to the case study, using a methodology that could readily be transferred to
another location if required. Prior to carrying out analysis of observed climate data, a review of
existing test methods and standard protocols was completed, in order to generate a contextual
picture of the range of flow rates currently being used to test for wind driven rain exposure. The
empirical measure of wind driven rain (WDR) having first been proposed by Lacy (1977) [15]
the relationship has since undergone a process of iteration [16] until its current accepted form
[17]. The relationship describes the translation of rainfall into WDR using a vector relationship,
taking account of wind speed to determine a rate of rainfall that would theoretically impact on
a vertical façade of a building, typically given in mm/hour. This value therefore translates into
a flow rate that could be specified in a test protocol assessing WDR impact. However, existing standards and literature discussing this have not typically applied this relationship to specify test flow rates. 3 British Standard procedures and few investigations carried out in the field of building conservation address WDR impact on building facades provide test flow rates (Table 1). However, correlation to climate conditions is not yet a common feature of such procedures.

<table>
<thead>
<tr>
<th>Test</th>
<th>Flow Rate</th>
<th>Rainfall Rate</th>
<th>Test</th>
<th>Flow Rate</th>
<th>Rainfall Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>[18]</td>
<td>1.5 L/min</td>
<td>15 mm/hour</td>
<td>[10]</td>
<td>1L/min</td>
<td></td>
</tr>
<tr>
<td>[19]</td>
<td>2 L/min</td>
<td>21 mm/hour</td>
<td>[21]</td>
<td>2L/test</td>
<td></td>
</tr>
<tr>
<td>[20]</td>
<td>0.5 L/min</td>
<td>4 mm/hour</td>
<td></td>
<td></td>
<td>Not Correlated</td>
</tr>
</tbody>
</table>

This investigation looks to build upon these existing protocols by developing a more explicit derivation of the flow rates used, such that confidence in the representation of the flow rates can be optimised. The strategy was to design a means of calculating flow rate applicable for a specific site, using a method that could be translated to other sites in order to similarly find representative values for those locations. This could then be applied in the laboratory to a construction system determined using assessment of buildings at the site, such that the impact (and hence risk) at the site could be determined (Figure 1).

From the case study location of Tewkesbury a long term precipitation data set was obtained from the Met Office’s MIDAS system, and this was used to determine the long term average daily precipitation total for the site, which was determined as 36 mm/day. This was then used in conjunction with the 2m/s wind speed, specified as generating “wetting conditions” in BS 15927-3 [22] and input into the WDR equation to derive the average conditions for the site. This gave a daily total value, which was then required to be translated into a pattern of wetting and drying, the design of which was drawn from work at the Met Office [23] analysing the relationship between rainfall intensity and duration, and this was used to define the upper threshold for the flow rate used in the weathering procedure.

![Figure 1. Route map demonstrating weathering sequence design process](image)

To encourage wetting of the wall the water is dispersed at the slowest feasible rate to allow for the test length to remain feasible and for the continual 24 hr running of the test to be promoted.
This ultimately produced a wetting-drying cycle of: 40 min of wetting, giving a flow rate of 0.4 L/min, followed by a 2 hr and 20 min period of drying. The water was applied to the face of the specimen using a spray nozzle from which a combination of air and water was dispersed, representative of the wetting by rain droplets carried horizontally by wind. Mechanical tests were carried out on individual specimens after 100 and 200 cycles respectively. After the first 100 cycles of the 200 cycle test the specimen was dried to original weight before a second run of cycles was implemented. The assessment carried out in order to determine the test flow rates demonstrates that the earlier test protocols have tended to overestimate the flow rates required to replicate these types of wetting events, although the decreasing trend in flow rate suggests that the validity of such procedures is gradually improving, to which end this sequence design also contributes.

3. Laboratory programme

3.1. Specimen design and initial testing

Three masonry specimens were constructed using the reclaimed bricks and fresh non-hydraulic lime mortar. Among the reclaimed bricks available on the market, older, narrower, less dense and more absorbent bricks were chosen for being more vulnerable from the perspective of the test programme. The brick type selected was manufactured in Bridgwater, Somerset in the early 19th cc, with average dimensions 230 x 105 x 65 mm, and an average dry density of 1600 kg/m³. A test to determine the initial rate of absorption was carried out in accordance with BS EN 772-11 [24], and the specimens were found to have an average absorption of 16%. These bricks have therefore been classified as Category II, HD, Group 1 clay units of low durability [25, 26].

In order to determine compressive strength of whole bricks testing of a sample of 12 bricks was carried out in accordance with [25]. The loading rate was 3600 N/second, with capping provided by dense engineering cork to ensure even loading across the surface of the brick. The sample yielded an average compressive strength of 25.2 MPa, and a standard deviation of 2.4 MPa.

The mortar was a non-hydraulic mix, selected as a representation of the historic air lime typically used in historic masonry within the UK during the 13th to 17th cc [27], presenting an opportunity to study a mortar especially vulnerable to exposure to moisture due to its inherent softness and high absorption [28]. The mortar used had a traditional 3:1 ratio of aggregate to lime, mixed with pure lime putty and a combination of both sharp and soft sand. The masonry specimens were of dimension 490 x 390 x 120 mm thick, constructed of a total of 12 bricks laid in a stretcher bond, with a single skin of masonry (Figure 2 left). The bricks were laid wet with a 10mm mortar bed and the wallettes were cured for a total of 18 months prior to testing to ensure the maximum strengthening of the mortar and bonding. Three specimens were constructed in total; one specimen was tested unweathered to produce a datum. The 2nd and 3rd specimens were tested following 100 and 200 cycles of weathering respectively (Figure 1).
Prior to testing of the masonry specimens using the weathering sequence, individual bricks were exposed to the same weathering process. It was intended to also undertake the same tests on prisms of the mortar, however unfortunately the samples collapsed during the weathering process. Although this therefore did not yield any data for the analysis, their collapse is in itself a finding of the vulnerability assessment. The cyclic weathering of the bricks was an enhanced test, in that each brick was fully submerged for a period of 40 min, before being dried in the oven for 2 hr and 20 min at 40°. On average the moisture content reached after 40 min of submersion was 6% and after drying the bricks were returned to their original weight. It is appreciated a higher amplitude of fluctuation of moisture is likely to have occurred than through exposure to spray at 0.4 L/min, however the same frequency of cycling was maintained. Three cycles were completed in a day, and overnight the bricks were maintained at ambient temperature and humidity. A total of 50 cycles were completed before compression testing.

Six specimens were tested in compression according to [25] in a dry state following the cyclic weathering, producing an average compressive strength of 26.9 MPa and a standard deviation of 1.5 MPa. This finding would suggest that the cyclic weathering of the bricks had no impact upon their strength, assuming that the small increase in average strength exhibited is statistically insignificant. Testing after higher numbers of cycles may induce a more significant loss, and verification of this should form the focus of future work. This finding is also considered with testing carried out elsewhere in the Parnassus project [29], which assesses the impact of prolonged exposure to moisture on bricks and demonstrates that on average up to 43% of strength can be lost in bricks tested wet after 72 hours of submersion, where moisture content is determined by weight increase. Testing of bricks in this way is more representative of flood events or prolonged saturation due to capillary rise and highlights that this hazard may prove to be more significant for bricks than the WDR simulated by the cyclic weathering.

3.2 Masonry testing

The three masonry specimens were subject to the weathering sequence as in Figure 1, and then were dried to their original weight prior to testing under combined compression and lateral loading. This was to simulate the loading that an infill panel in a timber frame is likely to experience during a WDR event, when wind loading of the frame could potentially set up a racking process. This is reflected in the test procedure used for the masonry specimens, which takes reference from the standard test for determining racking strength of timber frames [30].
For each specimen a lateral load was cycled incrementally up to failure, in stages of 2.5 kN. The load was applied for 300+/−60 seconds, and at each level the load cycle was repeated 3 times. A vertical uniformly distributed load of 5+/−0.5 kN was applied, inducing a vertical compressive stress in the material of approximately 0.1 MPa, a value selected to represent loading of exposed on-site structures of similar construction. The displacement in the specimen was measured both vertically and laterally, in accordance with [31]. This was carried out with LVDT transducers mounted at fixed positions on the test rig frame and attached to the face of the masonry using brackets, which were screwed and glued into the bricks.

For each test the maximum lateral load that was withstood prior to failure was recorded, meanwhile Figure 2 (right) shows the lateral load-displacement relationship for the each of the three specimens. Shear strength was calculated in accordance with [26] and the results are displayed in Table 2 below. The maximum lateral loads withstood by the unweathered specimen and the specimen exposed to 100 cycles of wetting and drying are very similar. The shear strength reduction of the 100 cycled specimen is also very small at only 6.7%; meanwhile the 200-cycle specimen suffered a far greater loss of strength, representing a 51% reduction, by far the greatest impact of the test.

Table 2: Strength and stiffness characteristics of weathered and unweathered wallettes

<table>
<thead>
<tr>
<th></th>
<th>Unweathered</th>
<th>100 cycles</th>
<th>200 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{\text{max}} ) (kN)</td>
<td>10.8</td>
<td>10.6</td>
<td>4.2</td>
</tr>
<tr>
<td>Shear Strength, ( S ) (MPa)</td>
<td>0.105</td>
<td>0.098</td>
<td>0.051</td>
</tr>
<tr>
<td>Loss of ( S ) (%)</td>
<td>-</td>
<td>6.7</td>
<td>51</td>
</tr>
</tbody>
</table>

The failure mode of all the specimens was similar, with a diagonal path of failure developing entirely at the interface between the mortar and brick, travelling from the load point at mid-height on the left of the specimen towards the base of the specimen on the right hand side, (Figure ). In the case of the unweathered specimen initial cracks were observed after 2.5 kN of lateral load application, whilst by 10 kN substantial cracking existed across the whole sample of masonry were mobilised against one another. The 100-cycle specimen maintained a relatively intact façade until 5 kN of lateral load whilst mobilisation occurred at a similar load of 10.5 kN. The 200 cycles specimen exhibited initial cracking at 2.5 kN, with a complete crack network across the masonry face established by 5.5 kN of load.

Figure 3. Failed masonry wallette showing location and extent of shear crack
4. Discussion

The data collected from these tests, along with visual evidence of the failure mechanism in the masonry, suggests that the difference in impact between the 100 cycle test and 200 cycle test is significant. The drying that occurred between the first and second 100 cycles in the 200 cycle test is likely to have contributed to this, although some alteration of the bonding of the masonry did occur after 100 cycles, as is demonstrated by the changing crack pattern. The fact that this decay did not occur after cyclic testing of the bricks suggest that the loss of strength exhibited by the masonry is almost exclusively as a result of loss of bond strength and reduction in strength of the mortar itself. A shear strength test tends to highlight loss of capacity in the mortar bonds, which supports the theory that the mortar is the material that has suffered most from the wetting and drying regime, as the wetting and drying cycle of the mortar is likely to be of greater amplitude than in the bricks, considering this is the preferential route for moisture ingress.

The results of the prolonged wetting and cyclic wetting tests on bricks demonstrate the different impacts of different weathering conditions, and highlight that brick does exhibit varying degrees of recoverability when exposed to these types of climate events. The results suggest that the hazard posed by wind driven rain to bricks is considerably less than that posed by flooding and saturation of this material, i.e. cyclic wetting is less hazardous than prolonged wetting. The result is a positive finding from the perspective of cultural heritage preservation, as it means that those climate events that instigate a wetting and drying cycle in the material, which are considerably more frequent than floods, are less damaging, and hence the risk is lower. The findings should be validated through further testing of different examples of historic brick however, as they are can be highly varied in terms of physical and chemical composition. Furthermore, significantly higher numbers of wetting and drying cycles may induce a loss, however further testing on this individual material is beyond the scope of this investigation.

This study showed that wetting and drying can be critical to masonry with historic bricks as it induces high levels of shear strength reduction after 200 cycles. Tests on individual materials showed that bricks are comparatively resilient to this impact, whilst the mortar suffered most from this weathering regime, which is in line with previous studies [32]. The fact that the reduction in shear strength is only 7% for the first 100 cycles in contrast to 51% after another 100 cycles shows that the rate of the strength reduction greatly increases after a relatively flat initial variation.

A monitoring system was implemented on the façades of a number of buildings studies as part of the Parnassus project, with a range of indoor, outdoor and in-wall temperature (T) and relative humidity (RH) sensors, in conjunction with rain gauges and anemometers, with the aim of quantifying the hygrothermal loading to which they were exposed [33,34]. The data obtained from monitoring was further analysed in order to understand how the findings of this lab test scheme translate into the actual buildings that have been studied in Tewkesbury. In one year from May 2011 to May 2012, on the most exposed southwest façade of one of the case study buildings in Tewkesbury, Abbey Mill, a Grade II listed, 4 storey brick masonry building from the late 18th century, there has been one episode of WDR exposure that lasted equal to or longer than 40 min, which is the wetting duration used in the lab tests. Therefore, one can conclude that cyclic wetting and drying as defined by the lab tests is not a frequent action affecting the building under investigation.
Further, as seen from Figure 3 during this precipitation episode the outdoor RH values rise considerably, while for the in-wall RH the associated increase is around 5% from approximately the maximum value of 65% to 70%. On the other hand, it can be also seen the both the peaks and the nadirs of the outdoor RH and T fluctuations are followed by in-wall fluctuations almost without any time lag, but with a lesser degree of fluctuation. Therefore, the case study building can be said to be considerably resilient to cyclic wetting and drying action not only because of the rarity of such phenomenon, but also because of the intrinsic material properties that result in the dissipation of the extent of outdoor fluctuations.

5. Conclusions
The results show that the experimental weathering regime used here can result in significant degradation in the shear strength of the masonry, and that mortar is particularly vulnerable against this action. On-site monitoring showed that in one year, between May 2011 and May 2012, only one precipitation episode that produced wind driven exposure comparable to the wetting action defined by the testing programme. Whilst variation in the annual climate conditions must be considered, it is a fair conclusion that the building could have been exposed to more than 200 such cycles in its lifetime of approximately 300 years. As such the exposed and non-refurbished sections would have undergone shear strength degradation of the scale quantified by these experimental tests.

However it is currently uncertain how much the strength reduction indicated by the experimental tests is dependent on the length of the drying periods. In the experimental tests this period was less than three hours, while the data collected during the monitoring period suggest that on-site conditions can extend drying conditions up to a year. In this respect shear strength degradation on site may follow a different pattern of loss, and the effect of drying
conditions needs to also be quantified before a complete appreciation of the weathering impact can be achieved.

This study aims at understanding the response of historic brick and masonry specimens to a series of weathering and mechanical tests within the context of wider work carried out at a case study location. The work highlights the value of designing a weathering regime that can more closely replicate the weathering processes taking place in-situ. In this way the data collected in this experimental programme is shown to be suitable for use in contextual analysis of individual historic masonry case studies, with respect to climate change impact and the associated alteration of wetting regimes. Despite the limited correlations made here, the difference between the weathering sequences used for testing purposes and observed on-site has be quantified for future work.

References
INFLUENCE OF pH DURING CHEMICAL WEATHERING OF BRICKS: LONG TERM EXPOSURE

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Abstract
Within the framework of environmental weathering of bricks in historical structures, this study focuses on new bricks currently employed for restoration projects. The bricks were subjected to an accelerated chemical weathering test by immersion in solutions with pH ranging from 3 to 13 for different lengths of time up to 432 days, data to 288 days are presented since the project is still ongoing. The study analyzed the changes of pH induced in the solutions by the presence of the bricks (this also served to adjust the pH to the intended value), as well as the concentration of various ions extracted from the bricks over time. As the bricks were taken out at the different times, their capillary absorption curves were determined, followed by a vacuum saturation with water for the determination of the open porosity, as well as the density. Finally, a 24 hour total immersion in water was also carried out proving to be practically the same as achieved after the capillary absorption rate stabilized after 6 hours in this test. The results obtained showed that the two main deterioration mechanisms are the ion-exchange at acid pH, and the alkaline corrosion undergone particularly at pH 13.

1. Introduction
The bricks used in this study are those currently employed for restoration projects, such as at the fortress walls surrounding the Royal Castle of Kronborg at Helsingør—made famous by Shakespeare in Hamlet—which was added to the UNESCO World Heritage List in 2000. The restoration started some 20 years ago and is still ongoing. So far there has been no indication of initial weathering of these bricks and none have been replaced according to the supervisory architect.

Historic brick masonry buildings have a long service life during which they can deteriorate, for example from acid precipitation [1,2]; or salt crystallization [3-5]. This will entail repairs and
treatments for their conservation, i.e., desalination [6,7]; or repointing [8-10]. While many studies have focused on mechanical failure of brick masonry materials, the slower chemical deterioration has only been explored to a limited extent. Many examples have documented how the wrong choice of materials for repairs results in chemical induced deterioration in the original material [9,11,12]. But because this is a slow process it has not received the attention it deserves.

In a preliminary large scale study [13] a correlation could be established between the weathering of fired clay bricks exposed to water with acid or alkaline pH and the glass phase theory [14-16]. However, several results were puzzling so the study was repeated and extended to include a highly alkaline solution (pH 13) and immersion lengths to 288 and 432 days. Since during the preliminary study it was noted that the pH of the solution changed over time, here the pH of the solutions was monitored regularly and regulated by addition of sulfuric acid and/or sodium hydroxide and data up to 340 days is reported.

2. Materials and Methods

2.1 Brick
The bricks used in the study are produced by Falkenløwe A/S, in Sønderburg, for restoration of historic brick structures. They are generally called Munkesten because they have the dimensions of old traditional Danish bricks (~ 28x7x14 cm) [17]. The medium red colored bricks were chosen for this study and specimens of approximately 11x5x5 cm, were cut from the center of the brick.

2.2 Weathering
The brick specimens were totally immersed in solutions having different pH values and varying immersion times at about 20°C. A total of 30 specimens were used, with 5 specimens immersed in six solutions with pH of 3, 5, 7, 9, 11 and 13 in covered vats. After 24 days, 1 specimen was removed for analysis from each of the different pH solutions; the subsequent 3 specimens were removed after 120, then 144, and last 288 days. After removal from total immersion the specimens were dried at 105°C prior to analysis. As reference samples, data from the previous study were used [13, 17].

2.3 Analysis
The changes in pH undergone by the different immersion solutions were monitored in order to adjust it weekly with a pH meter (MeterLab®CDM220). Samples from the various water baths were taken fairly regularly for analyses by ion chromatography (ICP optical Emission spectrometer Varian 720-ES). They were taken weekly both for the first 8 weeks and for the last 25 weeks, the last one corresponding to 340 days, but for reasons beyond our control, none were taken in between. After the samples were taken out of the various pH solutions, capillary absorption curves were determined following the standard RILEM procedure [18]. The samples, were placed in a closed container with water covering their base (5x5 cm) to about 3mm, and regularly weighed to monitor the capillary rise. The capillary water absorption coefficient (kg/m²sec¹/²) was determined while the amount of capillary water absorption (%w/w) was calculated from the capillary water uptake at 6 hours, since this is close to the maximum absorbed under these conditions. The samples were then dried again and subjected
to vacuum saturation with water and the open porosity and apparent density were determined according to standard EN 1936. After drying them again, they were totally immersed in water for 24 hours. The mass loss after each of these steps was determined for each specimen.

3. Results

3.1 Ion and pH changes of immersion solutions

For most ions the measured concentration oscillated initially but tended to stabilize after about 150 to 200 days. The average concentrations measured for these ions are summarized in Table 1. Some ions, such as Al$^{3+}$, Ca$^{2+}$, and SiO$_4^{2-}$ did not stabilize at all pH conditions, while Fe$^{2+/3+}$ and Ti$^{2+/3+}$ only had minimal dissolution at the extreme pH, i.e., 3 and 13. Table 2 summarizes the data for only those ions whose concentrations stabilized at some pH.

Table 1: Average concentration (in ppm) for ions when stabilized by 150-200 days. Standard deviation in italics between brackets.

<table>
<thead>
<tr>
<th></th>
<th>K$^+$ (mg/l)</th>
<th>Mg$^{2+}$ (mg/l)</th>
<th>Mn$^{2+}$ (mg/l)</th>
<th>Cl$^-$ (mg/l)</th>
<th>NO$_3^-$ (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td>19.0 (2.7)</td>
<td>18.6 (1.6)</td>
<td>0.87 (0.08)</td>
<td>5.5 (1.8)</td>
<td>17.1 (0.7)</td>
</tr>
<tr>
<td>pH 5</td>
<td>10.0 (1.4)</td>
<td>12.8 (0.7)</td>
<td>0.066 (0.009)</td>
<td>5.95 (0.22)</td>
<td>84 (16)</td>
</tr>
<tr>
<td>pH 7</td>
<td>12.8 (1.6)</td>
<td>7.4 (0.4)</td>
<td>0.012 (0.012)</td>
<td>8.38 (0.96)</td>
<td>1 (3)</td>
</tr>
<tr>
<td>pH 9</td>
<td>7.5 (1.1)</td>
<td>4.0 (0.4)</td>
<td>0.010 (0.011)</td>
<td>6.29 (0.18)</td>
<td>29.1 (0.9)</td>
</tr>
<tr>
<td>pH 11</td>
<td>12.4 (1.9)</td>
<td>0.08 (0.03)</td>
<td>0.008 (0.008)</td>
<td>6.12 (0.46)</td>
<td>0.37 (0.23)</td>
</tr>
<tr>
<td>pH 13</td>
<td>436 (60)</td>
<td>0.005 (0.01)</td>
<td>0.038 (0.014)</td>
<td>21 (10)</td>
<td>94 (37)</td>
</tr>
</tbody>
</table>

Table 2: Average stabilized concentrations (in ppm) measured with standard deviation in italics between brackets. Notes: (-) indicates that the concentration did not stabilize and either increased or decreased (see Figure 1); (0) indicates below detection level.

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<tr>
<th></th>
<th>Al$^{3+}$ (mg/l)</th>
<th>Ca$^{2+}$ (mg/l)</th>
<th>Fe$^{2+/3+}$ (mg/l)</th>
<th>Ti$^{2+/3+}$ (mg/l)</th>
<th>SiO$_4^{2-}$ (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td>(-)</td>
<td>(-)</td>
<td>1.51 (0.28)</td>
<td>0.004 (0.004)</td>
<td>111 (21)</td>
</tr>
<tr>
<td>pH 5</td>
<td>0.57 (0.23)</td>
<td>78.8 (8.0)</td>
<td>(0)</td>
<td>(0)</td>
<td>25.3 (5.8)</td>
</tr>
<tr>
<td>pH 7</td>
<td>0.08 (0.02)</td>
<td>55.2 (5.0)</td>
<td>(0)</td>
<td>(0)</td>
<td>16.9 (3.8)</td>
</tr>
<tr>
<td>pH 9</td>
<td>0.06 (0.02)</td>
<td>(-)</td>
<td>(0)</td>
<td>(0)</td>
<td>14.9 (3.5)</td>
</tr>
<tr>
<td>pH 11</td>
<td>1.17 (0.27)</td>
<td>7 (11)</td>
<td>(0)</td>
<td>(0)</td>
<td>33.6 (6.3)</td>
</tr>
<tr>
<td>pH 13</td>
<td>(-)</td>
<td>0.8 (2.4)</td>
<td>0.17 (0.06)</td>
<td>0.058 (0.008)</td>
<td>(-)</td>
</tr>
</tbody>
</table>

Figure 1 shows the plots of the concentration changes for the most relevant pH for Al$^{3+}$, Ca$^{2+}$ and silicate ion. While the concentration of Al$^{3+}$ increases significantly from pH 3 to pH 13, the concentration of Ca$^{2+}$ decreases with increasing pH, and for silicate ion, it is relatively low.
at acid pH, decreases to a minimum at pH 9 and increases for pH 11, reaching concentrations that oscillate between 1500 and 2500 ppm at pH 13.

Figure 1. Left: Changes in Al$^{3+}$ concentration at pH 3 and 13. Center: Equivalent curves for the Ca$^{2+}$ at pH 3 and 9; these curves showed some spikes that were attributed to pH changes and therefore not included. Right: Changes in SiO$_4^-$ concentration at pH 3 and 13.

For solutions with pH 3 to 7, the pH increases initially —over the first 50 days—, with pH 3 having the highest increase (occasionally reaching pH 7); followed by pH 5 (occasionally reaching pH 7); and then pH 7 (occasionally reaching pH >8). On the other hand, the alkaline solutions show an initial decrease of the pH, with pH 9 showing a decrease to pH 8; followed by pH 11 that initially reaches pH 9; and for pH 13 which has a minimal decrease. The pH of these solutions subsequently stabilized between 100 and 300 days and the data dispersion is smallest for pH 13 and 11, with the highest values corresponding to pH 5 and 7. Figure 2 shows the pH values measured prior to adjustment and the changes in the concentration of Na$^+$ not including those for pH 13 because it ranges from an initial 7000 ppm to around 25000 ppm (7 g/l to 25 g/l).

Figure 2. Left: Measured pH values prior to its adjustment. Note that after 100 days the pH remains fairly stable and that pH 9 is below pH 7. Right: Na$^+$ concentration in the immersion solutions (excepting that for pH 13 which reaches over 50 times the maximum value shown).

Since to keep pH fairly constant, H$_2$SO$_4$ and NaOH were added, the data for SO$_4^{2-}$ are not reported. The pH was monitored regularly, and initially (24 to 161 days) for solutions having pH 3 to 7, acid was used to maintain the pH. For the case of pH 7, only after 165 days was NaOH occasionally added to keep it constant; of the 34 times where pH was adjusted, only 9 times required addition of NaOH.
3.2 Weight changes of the samples
The samples were weighed initially and subsequently, after drying, when they were taken out of the immersion solutions. They were also weighed after each of the subsequent tests. Figure 3 shows the weight changes after immersion for the specified time; the uncertainty in the measurements is about 0.004%. After 24 days, all samples increased in weight except those at pH 9 and 11 (Figure 3 left). Samples at pH 9 were the ones that lost or gained minimal weight (0.015%) while those at pH 11 only lost weight initially (0.014%) and subsequently started gaining weight (Figure 3 right). Those that changed most corresponded to the extremes: pH 3 increased in weight for the first two immersion times (0.022 and 0.012%) and then lost weight significantly (0.014 and 0.141%). The same pattern was observed for pH 13, initial weight increase (0.161 and 0.061%) and subsequent decrease (0.420 and 0.668%). To be noted is that efflorescence developed mainly on samples immersed at pH 13, and to a lesser extent, for those at pH 11. The initial weight increase suggests the presence of soluble salts that might have been retained in the sample during immersion in pH adjusted water (with H2SO4 and/or NaOH).

![Figure 3. Percent weight change of samples after immersion at different pH for various time lengths, plotted as a function of time or pH. Uncertainty in the measurement is about 0.004%.](image)

3.3 Capillary absorption test
The capillary absorption coefficient, CAC [kg/m².sec¹/²], also referred to as water absorption coefficient (WAC), was calculated from the trend line of the initial straight line. Table 3 gives the average values for the CAC at the different pH and immersion times, as well as that for the reference [13].

<table>
<thead>
<tr>
<th>pH</th>
<th>CAC [kg/m².sec¹/²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.39(0.02)</td>
</tr>
<tr>
<td>5</td>
<td>0.39(0.01)</td>
</tr>
<tr>
<td>7</td>
<td>0.48(0.09)</td>
</tr>
<tr>
<td>9</td>
<td>0.51(0.04)</td>
</tr>
<tr>
<td>11</td>
<td>0.52(0.05)</td>
</tr>
<tr>
<td>13</td>
<td>0.46(0.02)</td>
</tr>
</tbody>
</table>

For the case of pH 7, the data show an increase in the average obtained for 24 and 120 days (0.40 kg/m².sec¹/²) and that after 144 and 288 days of immersion (0.55 kg/cm².sec¹/²) as seen in Figure 3 and in the significant higher standard deviation obtained reflecting the changes required to keep a steady pH (initial 165 days with H2SO4 and subsequently a few times with NaOH as mentioned). The CAC obtained in acid solutions is slightly lower than that at pH 7.
which in turn is lower than the one measured in alkaline solutions suggesting an increase in porosity through alkaline corrosion of the matrix.

The amount of water absorbed by capillarity after 6 hours of the CA test is very similar to that absorbed after 24 hour total immersion in water for all samples. This amount varies with exposure time and pH of the solution, and the same trend is observed for the amount of water absorbed by vacuum impregnation as discussed in the subsequent section. Figure 5 shows the percent weight increase for the samples after 6 hours absorption during the capillary absorption test. Samples from immersion in pH 3, 9, and 13, show an increase in absorption with time. Sample from pH 5 shows a minimal decrease, and that of pH 11 the minimum change, while that for pH 7 has an initial decrease followed by an increase. Also shown in this figure is a graph of the average values and data spread. The spread of the data is largest for pH 7 and minimum for pH 11. The data spread (approximately twice the standard deviation) ranges between ±0.4 and ±1 for most samples, except that from pH 7 for which it is ±2.

Figure 4. Left: Capillary absorption coefficients for pH 5, 7 and 13 having significantly different standard deviations. Right: Maximum, minimum and average CAC values obtained at the various pH; the spread of data is slightly more than twice the standard deviation.

Figure 5. Left: Amount of water absorbed by capillarity after 6 hours of CA test at the various pH. The most regular patterns are obtained at pH 9 and 11. Right: Maximum, minimum and average values obtained at the various pH and for the reference.
3.3 Apparent density and open porosity
The average apparent density of the samples immersed in solutions between pH 3 and 7 ranged between 1778 kg/m³ at pH 3, and 1774 kg/m³ at pH 7, while reference samples were 1780 kg/m³ (±27) [17]. The lowest standard deviation was obtained for pH 5 1776 kg/m³. Figure 6 shows this data graphically and as well as that for open porosity. Average open porosity was around 33.9% for samples in solutions between pH 3 and 5; 33.7% for pH 7; and 32.2% for the alkaline pH, while, the reference sample was 33.0 % (± 1.9) [17].

![Figure 6. Left: Apparent density (kg/m³), average standard deviation ±18. Right: % Open porosity, average standard deviation ±1.](image)

For pH 9, both density and porosity show a slight initial decrease that remains fairly constant with longer immersion times. On the other hand, for pH 13 there is a regular decrease in density and increase in open porosity. This reflects the relative mass loss (final weight after all tests and initial weight) of the sample for the brick specimens depending on the pH to which they were subjected (Figure 7). It is clear that specimens immersed at pH 5, 7, 9 and 11 show a minimum mass loss (Figure 3 right), whereas the sample at pH 3 shows a slightly higher loss (0.4% w/w), while samples in pH 13 underwent a significant mass loss (2% w/w).

![Figure 7. Mass loss (%) over time during immersion at different pH solutions.](image)

4. Discussion and Conclusions
The immersion of bricks at different pH and for varying intervals showed that the concentration of some leached ions, i.e., K⁺, Mg²⁺, Mn²⁺, Cl⁻ and NO₃⁻, stabilized after a time. Initially, 5 samples were immersed in each solution, and then they were removed one at a time, so that by
144 days only 2 samples remained. While for Ca^{2+}, Mg^{2+} and Mn^{2+} the highest concentration was obtained at pH 3, as expected from the ion-exchange mechanism [15,16,19] and reflected in the mass loss over time (Figure 7), the highest concentration of K^+ was obtained at pH 13, being about twenty times higher than for pH 3. This suggests that the K^+ results from alkaline corrosion of the siliceous phase, glassy or ceramic, and the high extraction of Al^{3+} and silicate ion at pH 13 would appear to confirm this hypothesis [14]. The anions, Cl^- and NO_3^- were mostly extracted at pH 13, possibly also due to the same mechanism. The ion exchange of Al^{3+} at pH 3 has been found to proceed beyond 288 days, whereas that for Ca^{2+} had stabilized (Figure 1). In pH 13, minimal Ca^{2+} was detected and Al^{3+} was found to stabilize around 80 mg/l by 340 days. On the other hand corrosion of the siliceous phase was measured between 288 and 340 days (Figure 1) and is expected to increase as this phase constitutes 71-87 %w/w in a historical brick [1].

The weight of most of the samples increased after immersion in the solutions (Figure 3), reflecting the possible formation of soluble salts, especially at alkaline pH where uniform efflorescence formed on brick surfaces from pH 13, lesser at pH 11. These were found to be Na_2CO_3 since the Na^+ remaining from pH adjustment would react with CO_2 from the air.

The main objective of the study was to assess the effect of pH on the brick matrix, so average values were calculated from the four results over time per pH for the tests, as only one specimen per pH per immersion time was available. Therefore, the corresponding calculated standard deviation also includes variation from the effect of exposure length. This rather unorthodox procedure was used as a first approach in the analysis of the data. For the case of the capillary absorption coefficient, the average CAC at pH 7 is similar to that of the reference sample, but its standard deviation is higher, possibly due to pH fluctuations resulting from the pH adjustment over the length of the experiment, initially with acid (up to 165 days), and then occasionally with NaOH. These additions could explain the increase in the average value obtained between those calculated for the two first data points (0.40 kg/m^2.sec^{1/2}) and the last two (0.55 kg/m^2.sec^{1/2}). The CAC shows that capillary water absorption is slower in acid solutions compared to alkaline ones (Table 3, Figure 4) reflecting the alkaline corrosion by the brick/glassy phase in this environment resulting in an increased pore size.

The amount of capillary water absorbed after 6 hours is practically identical to that absorbed for these samples when totally immersed for 24 hours, indicating that most of the pore sizes in these bricks fall within the capillary range (1μm to 1 mm) [20] and correspond to about 70% of that absorbed under vacuum. The capillary water absorbed after 6 hours expressed as % open porosity (v/v) ranged from about 24.3% for pH 3 and 5, to 23% for pH 7, and 22.4% for pH 9 and 13, while pH 11 showed the lowest value of 20.9%. This agrees with the overall mass loss measured for these samples which for pH 3 and 13 samples follows the expected trend resulting from the two deterioration mechanisms (Figure 7L). For pH 11, a minimal mass loss occurs, while those at pH 5 and 9 show an initial mass loss followed by a slight weight increase between 120 and 144 days. The sample at pH 7 shows the same initial mass loss followed by a slow mass increase slightly above its original weight (Figure 7R). These patterns are similar to those observed for the amount of water absorbed after 6 hours capillary absorption (Figure 5R). These variations could also be attributed to differences in the individual brick specimens and is a point that requires further analysis.
Density and porosity of the samples varied over time during their immersion in acid or alkaline solutions. However, these changes fall within the standard deviations obtained for the reference sample. The clearest trend was observed for samples in pH 13, with a decrease in density and a corresponding increase in porosity with longer immersion times that can be attributed to the alkaline corrosion; in the words of Lewin and Charola [19] “as the porosity increases, the rate of deterioration also increases, both because of increased access of water and solutes to the interior, and the increased chemical reactivity of the decay products.”

Studies of brick and mortar combinations have shown that lime-water, i.e., Ca(OH)$_2$ solution migrating from mortar to brick results in an ion exchange between the Ca$^{2+}$ for Na$^+$ ions, and to a lesser extent for K$^+$ [21,22], a point that may be relevant for cement containing mortars as these may retain uncarbonated lime for at least a century [23]. Also, some cements may supply significant amounts of soluble sulfates and alkalis promoting formation of salts, e.g., Na$_2$SO$_4$, whose crystallization will contribute to brick deterioration [8].

The study has shown that bricks tested under rather forced conditions—one of the intrinsic problems when trying to accelerate slow damage mechanisms—resulted in some data that require further examination. For example, the unexpected changes found for samples at pH 7 in capillary water absorption after 6 hours (or 24 hour total immersion) between 120 and 144 days and which are also evident in the mass loss for samples in pH 5 to 11 (Figure 7). The project is still ongoing and it is hoped that further analyses will elucidate these questions.

In conclusion, chemical weathering is a slow but significant process for historic brick masonry over centuries of service life. To minimize the damage that could be introduced by required repairs with new bricks, these have to have compatible properties to the original and be as weather-resistant, hence the need for evaluating them.

References

SUITABILITY OF DIFFERENT PAINT COATINGS FOR RENDERS BASED ON NATURAL HYDRAULIC LIME

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(2) Instituto Superior Técnico (IST), Universidade de Lisboa, Lisbon, Portugal

Abstract
The paper intends to evaluate the behaviour of different paint coatings when applied on renders based on natural hydraulic lime and, thus, to aid in the selection of adequate paint solutions to be used in conservation interventions. For that, tests were performed on painted and unpainted specimens of hydraulic lime mortar and of blended lime putty-natural hydraulic lime mortar. Five different paint coatings were used: a limewash, a modified limewash with a commercial additive, two silicate paints and an acrylic emulsion paint (plastic paint). Results showed that the blended mortar was more influenced by the paint solutions than the natural hydraulic lime mortar. The limewashes proved to be the most suitable solutions for the tested mortars. The two silicate paints promoted quite different alterations on the mortars, which is indicative of the diversity of silicate paints available on the market. The plastic paint did not significantly alter the water absorption by capillarity nor the drying kinetics of the tested mortars, but somewhat hindered the water vapour permeability, and hence should be carefully considered.

1. Introduction
The repainting of historic buildings is a frequent action in the field of conservation and restoration of cultural heritage. However, the choice of an adequate paint coating still raises questions, in part due to the large variety of paint solutions available on the market that are too genericly specified for use in old buildings. An inappropriate paint solution can compromise the performance of old masonry walls, enabling the development of anomalies that affect the buildings durability.
The presence of water in buildings is considered normal, particularly in old buildings, since they are made of porous materials that can absorb water rather easily. For this reason, the paint system to be adopted should provide some protection against water ingress; not have a
hindering effect on the drying of the walls; and present a water vapour permeability compatible with that of the substrate [1].

Limewashes and silicate paints are frequently recommended solutions for historic buildings [1-3] because they have the advantage of being more "breathable" than most modern paints. Limewash is a simple and traditional inorganic coating based on a suspension of lime in water, with or without pigments, that has been used for centuries. More recently, to enhance adhesion and reduce the water absorption of these paint solutions, synthetic resins or additives of various types have been used. However, the inclusion of such substances can originate limewashes with an unpredictable behaviour. Silicate paints are based on an inorganic binder, usually potassium silicate or sodium silicate. The hardening of these silicate compounds happens as a silicification process that includes a chemical reaction with carbon dioxide from the air and with mineral components of the substrate (slaked lime or quartz). The resulting coating is porous and permeable to water vapour. Nevertheless, silicate paints usually require the removal of all earlier paint material, are largely irreversible once applied [4] and can often originate problems after application [5].

On the other hand, common “plastic” paints have been a frequently used paint solution in conservation interventions of historic buildings [5, 6], even though they can impose a barrier to water flow, preventing the walls from “breathing” [7]. In the past few years, other types of paint solutions have emerged on the market and have been increasingly used in conservation interventions, such as those based on silicone resins (polysiloxane, acrylic or styrene-acrylic resins) and on hydro-pliolite resins [6].

The choice of an adequate paint coating must also take into account the specific characteristics of the underlying rendering mortar, since they influence one another. The majority of old buildings have renders based on aerial lime and it is generally assumed that in a conservation intervention the repair mortar should be similar to the old mortar in terms of composition and characteristics in order to achieve the required compatibility. Natural hydraulic lime has been considered by several authors to be a compatible material to use in repair mortars, since it leads to mortars with characteristics similar to aerial lime ones, but with moderately higher mechanical strength at early age [8-12].

Therefore, this work aims at studying the influence of different paint coatings on the behaviour of renders based on natural hydraulic lime and, thus, to aid in the selection of adequate paint solutions to be used in conservation interventions. In order to achieve that objective, a variety of tests were performed on painted and unpainted mortar specimens, using five different paint coatings: a limewash, a modified limewash with a commercial additive based on synthetic resins, two silicate paints and an acrylic emulsion paint (plastic paint). The paint coatings were applied on a natural hydraulic lime mortar and on a blended lime putty-natural hydraulic lime mortar.
2. Experimental work

2.1 Materials
A natural hydraulic lime mortar and a blended lime putty-natural hydraulic lime mortar, both with a B/Ag (binder/aggregate) ratio of 1:3 (volume) were used as substrates. The studied mortars correspond to the preliminary formulations tested in the experimental program that was carried out to support the selection of the materials to be adopted on the restoration of the façades of the National Palace of Queluz (Portugal).

A natural hydraulic lime (NHL 3.5 according to EN 459:2002 [13]) from Secil and a lime putty from Maxical, both commercial products, were used as binders. As aggregate, it was used a mixture of two siliceous sands, which differ mainly in particle size: APB60 has a particle size ranging mainly between 0.2 and 0.5 mm, while that of APB40 ranges between 0.2 and 1 mm. The aggregate was previously dried before the preparation of the mortars.

The hydraulic lime mortar (H) was produced with the volumetric proportions 1:2:1 (hydraulic lime:APB60:APB40) and the blended mortar (AH) with the volumetric proportions 1:1:4:2 (hydraulic lime:lime putty:APB60:APB40). To avoid imprecision in the mixing process, the B/Ag ratio by volume of the mortars was converted to weight. All mortar mixtures were prepared using the necessary water/binder (W/B) ratio to obtain a consistency, measured by the flow table test (EN 1015-3:1999 [14]), of 205±5 mm for the hydraulic lime mortar and 185±5 mm for the blended mortar. As so, it was used a W/B ratio of 1.23 in mortar H and of 1.46 in mortar AH.

The mortars were produced based on the procedures of NP EN 196-1:1996 [15], and were moulded into prismatic specimens with the dimensions 160x40x40 (mm) and 150x50x50 (mm), and de-moulded 7 days later. The mortar specimens were kept in a conditioned room at 20±2 ºC and 60±5% RH for two months, until testing.

Five different paint coatings, corresponding to solutions often applied in historic buildings, were selected:

i. Lw – Simple pigmented limewash that corresponds to the preliminary formulation tested in the experimental program that was performed to support the selection of the materials to be adopted on the restoration of the façades of the National Palace of Queluz (Portugal);

ii. ALw – Limewash Lw modified with Adical (5% in weight), a commercial additive based on synthetic resins, described as a product responsible for extending the lifetime of limewashes in terms of weather resistance, adherence and water absorption;

iii. SA – Silicate paint from a brand with great expression in the European market. It is described in its technical sheet as a paint system based on a binding agent combination of silica sol and potassium silicate for mineral substrates;

iv. SB – Silicate paint from a Portuguese company, described as a system with a primer and an emulsion of potassium silicate as principal binder;

v. PP – Plastic paint, ultra matt, described as an emulsion paint based on a styrene-acrylic dispersion, for application on exterior and interior walls.

The non-painted specimens will be designated as NP.
The paint coatings were applied on the top surface of the prismatic specimens by brush according to the manufacturers’ specifications, which are summarized in Table 1. The commercial paints were easily applied, since they presented a good flow, and the simple limewash was more difficult to apply evenly than the modified one. Seven days after application, the 150x50x50 (mm) specimens were cut into cubic specimens with the dimensions 50x50x50 (mm), for the water absorption by capillarity and drying kinetics tests. The 160x40x40 (mm) specimens were only used for the determination of the water vapour permeability and were cut into slabs of 40 mm side and 10±2 mm thickness before the application of the coatings.

Table 1: Application details of the paint coatings

<table>
<thead>
<tr>
<th></th>
<th>Number of coats</th>
<th>Dilution</th>
<th>Time between coats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limewashes (Lw and ALw)</td>
<td>4 crisscrossed</td>
<td>0%</td>
<td>24h air + 48h carbonation chamber</td>
</tr>
<tr>
<td>Silicate paint SA</td>
<td>2</td>
<td>0%</td>
<td>24h</td>
</tr>
<tr>
<td>Silicate paint SB</td>
<td>2</td>
<td>0%</td>
<td>24h</td>
</tr>
<tr>
<td>Plastic paint (PP)</td>
<td>3</td>
<td>1st coat –10% water; 2nd and 3rd coats – 5% water</td>
<td>12h</td>
</tr>
</tbody>
</table>

2.2 Experimental tests

The substrate mortars were initially characterized through the determination of the open porosity, saturation coefficient and water content after 48h in immersion. These tests were performed on at least 3 mortar specimens with the dimensions 50x50x50 mm³, after a curing time of 2 months. The open porosity of the mortars was determined following the procedures established on RILEM Test No. I.1 [16] and the saturation coefficient and water content after 48h in immersion were determined according to RILEM Test No. II.2 [16].

The evaluation of the suitability of the different paint coatings on the water transport properties of the hydraulic lime based mortars included the determination of the water absorption by capillarity, drying kinetics and water vapour permeability. These tests were performed on at least 3 unpainted and 3 painted specimens with each paint coating, after a curing time of two months and 7 days after painting. The water absorption by capillarity of the painted and unpainted mortar specimens was determined based on the procedures established on RILEM Test No. II.6 [16] and their drying kinetics was evaluated based on the procedures of RILEM Test No. II.5 [16]. Both tests were performed on 50x50x50mm³ specimens. The water vapour permeability was evaluated according to the procedures adopted by Ferreira Pinto [17], which are based on RILEM Test No. II.2 [16]. The test was performed on slabs of 40mm side and 15±5mm thickness. A detailed description of the test procedures can be found in [8] and [9].
3. Results and discussion

3.1 Porosity and water absorption

The open porosity, saturation coefficient and water content after 48h in immersion (W48h) of the substrate mortars are presented in Table 2. As can be seen, the tested mortars showed close open porosity and saturation coefficient values. Nonetheless, the blended mortar (AH) showed a slightly higher capacity to absorb water than the hydraulic lime mortar (A).

Figs. 1 and 2 present the average curves of water absorption by capillarity over time of the painted specimens of hydraulic lime mortar and blended lime putty-hydraulic lime mortar, respectively, and Table 3 presents the corresponding coefficients of water absorption (CWA) and asymptotic values (AV).

Table 2: Open porosity, saturation coefficient and water content after 48h in immersion (W48h) of the tested mortars

<table>
<thead>
<tr>
<th>Open porosity (%)</th>
<th>Saturation coef. (%)</th>
<th>W48h (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural hydraulic lime mortar (H)</td>
<td>24.7</td>
<td>88.1</td>
</tr>
<tr>
<td>Blended lime putty-natural hydraulic lime mortar (AH)</td>
<td>25.7</td>
<td>85.7</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)

**Figure 1.** Water absorption by capillarity curves of painted and unpainted specimens of hydraulic lime mortar

![Figure 2](image2.png)

**Figure 2.** Water absorption by capillarity curves of painted and unpainted specimens of blended lime putty-hydraulic lime mortar

All water absorption curves have an initial linear section that suddenly develops towards an asymptote, which usually indicates that the pore network is not quite heterogeneous, nor poorly interconnected. The blended mortar presented a higher initial water absorption rate (higher CWA) and amount of water absorbed by the end of the test (higher AV) than the hydraulic lime mortar. The lower porosity and, possibly, the smaller pore diameter of the hydraulic lime mortar when compared to the blended mortar, as evidenced by Silva et al. [8, 9], could explain the
slower water absorption. The influence of the paint coatings on the water absorption by capillarity was clearly more notorious on the blended mortar, were they were responsible for a steeper reduction of the initial water absorption rate and of the total amount of water absorbed.

The specimens with the simple limewash (Lw) presented the highest capillarity absorption rates of all the painted specimens, introducing a negligible resistance to water ingress, irrespective of mortar type. The synthetic resin present in the modified limewash (ALw) reduced the coefficient of water absorption in both mortars and the asymptotic value in the blended mortar. The silicate and the plastic paints (SA, SB and PP) were the paint coatings that reduced more significantly the coefficient of water absorption by capillarity, Table 3. However, in terms of total water absorbed, the silicate paints showed a very heterogeneous behaviour. In mortar H the silicate paint SB led to the highest amount of water absorbed. On the contrary, in mortar AH, it was the silicate paint SB that originated the lowest amount of water absorbed. This means that silicate paint SB merely delayed the water ingress in the hydraulic lime mortar, as evidenced by the water absorption curve, Fig. 1, while in the blended mortar it also provided some protection against water entry. The plastic paint led to a high asymptotic value, but delayed water from entering the substrate, particularly when applied on the blended mortar, Fig. 2.

Table 3: Coefficients of water absorption by capillarity (CWA) and asymptotic values (AV) of the tested painted and unpainted mortar specimens

<table>
<thead>
<tr>
<th></th>
<th>Natural hydraulic lime mortar (H)</th>
<th>Blended lime putty-natural hydraulic lime mortar (AH)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CWA (kg.m(^{-2}).s(^{1/2}))</td>
<td>AV (kg.m(^{-2}))</td>
</tr>
<tr>
<td>NP</td>
<td>0.261</td>
<td>10.10</td>
</tr>
<tr>
<td>Lw</td>
<td>0.267</td>
<td>9.88</td>
</tr>
<tr>
<td>ALw</td>
<td>0.209</td>
<td>10.04</td>
</tr>
<tr>
<td>SA</td>
<td>0.195</td>
<td>9.67</td>
</tr>
<tr>
<td>SB</td>
<td>0.191</td>
<td>10.65</td>
</tr>
<tr>
<td>PP</td>
<td>0.203</td>
<td>10.08</td>
</tr>
</tbody>
</table>

3.2 Water vapour permeability
The average and maximum and minimum values obtained for the coefficient of water vapour diffusivity (CWVD) of painted and unpainted specimens of hydraulic lime mortar and of blended lime putty-natural hydraulic lime mortar are presented in Figs. 3 and 4, respectively. As shown in the graphs, the painted and unpainted mortar specimens of blended lime putty-hydraulic lime mortar presented a slightly superior permeability to water vapour than their hydraulic lime mortar counterparts. Moreover, the paint coatings had a greater influence on the water vapour permeability when applied on the blended mortar, which might stem from a deeper penetration of the paint into the larger pores of the blended mortar.

The plastic paint (PP) was responsible for the highest reduction of the water vapour permeability in both mortars, which allows concluding that this type of paint constitutes an obstacle to the passage of water vapour. On the other hand, the silicate paint SA did not
promote any relevant alteration on the water vapour permeability of the tested mortars. The silicate paint SB and the limewashes (Lw and ALw) revealed a similar influence on the water vapour permeability of both mortars, leading to a slight reduction of CWVD values. The abovementioned tendencies were observed in both mortars.

Figure 3. Coefficients of water vapour diffusion (CWVD) of painted and unpainted specimens of hydraulic lime mortar

Figure 4. Coefficients of water vapour diffusion (CWVD) of painted and unpainted specimens of blended lime putty-hydraulic lime mortar

3.3 Drying kinetics

Figs. 5 and 6 illustrate the average water contents over time of the tested painted and unpainted mortar specimens and Table 4 presents the corresponding initial drying rates (IDR) and drying index (DI) values.

The drying process of a porous material saturated with water can be divided in three stages. The initial stage of the drying process depends on the external conditions and the evaporation occurs under constant rate (initial drying rate) until the critical moisture content is reached, which takes place when the liquid water can no longer be supplied to the surface by capillary transport. After that, the water is mostly transported by capillarity, beneath the wet front, and by vapour diffusion, ahead of the wet front. During the final stage, the drying rate is very low and almost constant [18].

Both mortars revealed very similar drying kinetics, with the blended mortar having a slightly faster initial drying rate, a lower duration of the initial drying phase and a higher critical moisture content as well as final water content. The less homogeneous pore size distribution expected for the blended mortar might justify the higher critical moisture content [19], while the slightly faster initial drying rate is probably related to a higher porosity and pore size, a conclusion that is in conformity with its higher water absorption by capillarity coefficient.

The effect of the tested paint coatings on drying was not very significant, especially when the substrate was the hydraulic lime mortar. The specimens with the simple limewash (Lw) exhibited drying kinetics very close to those of the unpainted mortars, with a slightly lower initial drying rate. The samples with the modified limewash surprisingly presented the fastest...
drying, with initial drying rates higher than those of the unpainted specimens. This result is in accordance with what was described in the literature, namely that limewashes accelerate the drying process because they create a larger effective surface of evaporation [20, 21]. The difference observed between the behaviour of the two limewashes (Lw and ALw) is probably related to application: the modified limewash was easier to apply, forming a more homogenous film on the surface of the substrate, due to the presence of the synthetic resins.

Table 4: Drying index (DI) and initial drying rate (IDR) of the tested painted and unpainted mortar specimens

<table>
<thead>
<tr>
<th>Natural hydraulic lime mortar (H)</th>
<th>Blended lime putty-natural hydraulic lime mortar (AH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>IDR (g.cm(^{-2}).h(^{-1}))</td>
</tr>
<tr>
<td>NP</td>
<td>0.21</td>
</tr>
<tr>
<td>Lw</td>
<td>0.20</td>
</tr>
<tr>
<td>ALw</td>
<td>0.19</td>
</tr>
<tr>
<td>SA</td>
<td>0.21</td>
</tr>
<tr>
<td>SB</td>
<td>0.22</td>
</tr>
<tr>
<td>PP</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The drying kinetics of the specimens with silicate paints SA and SB resembled that of the unpainted mortar specimens when applied on the hydraulic lime mortar. In the blended mortar, and similarly to what was verified for water absorption, the silicate paints led to very different results: the specimen with silicate paint SA dried more rapidly than the non painted specimen, while the specimen with silicate paint SB presented a rather slower drying process. It can thus be concluded that silicate paints must be carefully considered because their effect on the
absorption and drying behaviour of a substrate can be different, depending on the characteristics of the silicate paint and of the substrate. The heterogeneous behaviour of silicate paints has also been highlighted by Brito et al. [6]. The plastic paint (PP) led to similar initial drying rates to those of the uncoated specimens, but to higher drying index values, probably because of its lower water vapour permeability, important feature in the falling drying rate stage, being the paint solution that hindered the drying process of the substrates the most.

4. Conclusions

The present work allowed concluding that paint coatings influence the substrates behaviour in the presence of water and that the morphological characteristics of rendering mortars affect the extent of that influence. The results showed that the blended mortar, formulated with natural hydraulic lime and lime putty, was more influenced by the paint coatings than the natural hydraulic lime mortar. This result can probably be attributed to a less homogeneous pore size distribution and the presence of larger pores in this mortar that facilitate the penetration of the paints.

All the tested paint coatings reduced the substrates water absorption, especially in the blended mortar. The two limewashes allowed a faster water absorption by capillarity than the other paints. Comparing the two limewashes, the modified one originated a higher reduction of the capillarity coefficient, but did not hindered drying. In fact, it improved the initial drying rate, possibly due to an increase of the effective surface of evaporation. The studied paint coatings did not impose a significant resistance to drying, presenting drying curves not very different from those of the unpainted specimens. Nevertheless, it was the plastic paint and silicate paint SB that hindered drying the most. The two silicate paints presented a heterogeneous behaviour in terms of water absorption by capillarity and drying kinetics, particularly when applied on the blended mortar. It can thus be concluded that the selection of this type of paints for conservation interventions should take into account the diversity of silicate paints available on the market, and that its performance can be significantly affected by the characteristics of the substrate. The plastic paint presented reasonable behaviour in terms of water absorption by capillarity and drying kinetics, but somewhat hindered the permeability to water vapour, which means that the use of this type of solution should be considered with caution, since it can be responsible for alterations of the position of the wet front and of the location of salt crystallization. Considering the water transport properties assessed, the results suggest that the simple and the modified limewashes are the most suitable paint coatings for the studied mortars.

Acknowledgements

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References


DETERMINATION OF MOISTURE DISTRIBUTION IN BRICK MASONRY WALLS

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Abstract

A dielectric probe developed for vertical soil moisture measurement was adapted for horizontal use in solid masonry walls. The instrument provided a detailed moisture profile of the wall in several positions. The moisture distribution over the cross section was determined and the source of moisture was identified. This methodology is suitable for in-situ experiments, but the use is limited by the invasive nature. The paper presents two cases: A 14th century building at Frederiksborg Palace was exposed to rising damp. Cement mortar joints were replaced with lime mortar to accelerate the natural drying of the masonry above ground. No effect of this intervention could be identified after one year. The source of moisture from below was probably too abundant to be counterbalanced by evaporation. A 15th century garden wall at Marielyst Palace was subjected to a vertical migration of water from an elevated terrain at the back side. A cement render at the front side protected the wall against wind driven rain, but reduced the evaporation of moisture from the wall. The wall should either have better protection against moisture from the back side, or a render which is more open to evaporation at the front side.

1. Introduction

1.1 The problem

Historic masonry walls are exposed to moisture from different sources such as wind driven rain or rising damp from the ground. It is not always easy to identify which is the dominant or to evaluate the effect of various interventions. The wall thickness of historic masonry is usually 50 – 100 cm, so moisture measurements at the surface do not give accurate information about the conditions inside the wall. A further complication is contamination with salts, which may have accumulated at the surface. The ionic content of the pore water will severely disturb the signal of most moisture meters and make surface measurements
unreliable. To conduct a detailed study of the moisture distribution in time and space, it is required to provide access to the inner parts of the wall.

1.2 Previous experience

Permanently installed sensors made of gypsum were used for monitoring the water content in brick masonry walls in Tirsted Church [1]. The sensors were embedded in the chancel wall at different heights and depths, and the electrical resistance was measured at regular intervals over a year. The advantage of this particular sensor is that the range of measurement responds well to brick masonry. Drying of the wall to the inside could be observed in winter, and the source of water was identified as wind driven rain rather than rising damp.

A dielectric probe was used to monitor the effect of dehumidification in Kippinge Church [2]. A description of the instrument is given below. The change in water content in the chancel walls was measured over four years. This instrument provided detailed moisture profiles over the entire cross section of the walls, and identified driving rain as the main source of moisture. There was a large difference between the water content in the north and south façade of the chancel. The predominant wind direction in Denmark is south-west, which may account for a stronger rain exposure to the south.

2. Method

2.1 The dielectric probe

A portable instrument developed for soil moisture measurements was used for this study. The probe was a type PR1/6 from Delta Devices Ltd. with 6 sensors mounted on a rod, connected to a meter HH2. Each sensor has two circular steel rings of 25 mm diameter with a 50 mm distance (figure 1). An electric field at 100MHz frequency is induced to measure the impedance around the probe. The amplitude of the signal depends on the dielectric property of the surrounding material, which is strongly related to the moisture content. The electric field is directional, so each measurement is repeated 3 times, each at a 120° turn of the probe.

2.2 Installation

During operation the probe was mounted in access tubes with a diameter of 27 mm. The tubes were permanently installed in horizontal holes drilled in the wall. The tube protected the probe during operation and prevented evaporation from the inside of the holes. A plastic cap inhibited ingress of wind driven rain through the holes. To avoid disturbance of the moisture distribution within the wall, the holes were drilled without the use of water for cooling. Nevertheless, the moisture content of the masonry was possibly influenced by the heat released during drilling. It may take several weeks for equilibrium to re-establish, but it is not likely that the moisture distribution is permanently altered by the installation.

2.3 Influence of air gap

A field calibration of the instrument concluded that the readings were very sensitive to air gaps around the access tube [3]. Therefore, the individual readings should mainly be used to study the variations in moisture content, and not be interpreted as absolute values. A calibration test of the influence of an air gap along the access tube was reported in [4]. A
cavity of one mm reduced the signal by 25\% and a 3 mm cavity gave a 50 \% reduction of the signal. It is difficult to achieve a perfect fit, so an alternative method would be to drill an oversize hole and use a filler to ensure perfect contact. In this case the suction curve of the filler needs to be equivalent to the masonry [5]. An air gap would also allow condensation of moisture in the case of a temperature gradient between the inside of the access tube and the masonry. In theory water could be distilled along the outside of the tube from a warm to a cold end. This process has not been further investigated.

### 2.4 Calibration
The instrument has several calibration options for different types of soils. The calibration for mineral soil was used, since there is no calibration for building materials such as brick or mortar. The probes accuracy is +/- 4 \% volume according to the manufacturer. The instrument is not sensitive to temperature within the range 0-40 °C, or to moderate ionic concentrations in agricultural soils. An electric conductance of the pore water less than 400 mS/m does not affect the signal. The ionic content of the pore water in a wall can be much higher, so a calibration test was performed with different salt concentrations [6]. Three different concentrations of sodium chloride were tested to resemble a moderate salt contamination often found in brick masonry walls. The influence of a moderate salt contamination was significant at any moisture content. A salt content of 2 g/kg raised the reading of the instrument by a factor of three, but it was still proportional to the actual water content.

![Figure 1. The dielectric probe mounted in the access tube during operation at Frederiksborg Castle.](image)
3. Case studies

3.1 Façade wall at Frederiksborg Castle

The castle is situated in a small lake in the town Hillerød in North Zeeland. The oldest parts of the building complex date to 1580. The walls are solid brick masonry made of soft fired clay bricks and lime mortar. Extensive reconstruction took place after a fire in 1865 with the use of hard fired bricks and cement mortars. The present case study deals with a cylindrical building with a wall thickness of approximately 70 cm (fig. 3). The building was heated and ventilated in winter.

The building had been used for a dwelling but was abandoned due to mould growth in the floor on the first level. The cement mortar was removed and the joints were repointed with lime mortar to accelerate drying of the masonry. A monitoring program was initiated to determine the distribution of moisture in the outer wall and to evaluate the effect of repointing. Access tubes were installed at three levels as indicated in figure 2. Some results from the west facing part of the building are presented below.

The initial moisture profiles were determined with a distance of 1 cm between each measurement (fig. 4). Every measurement consisted of three readings with a 120° turn of the probe. The directional readings were quite close towards the outside, but more scattered in depth. This may reflect a cavity along the access tube towards the inside. It is difficult to drill a precise hole with a hand held drill. At the 140 cm profile there were a drop in the water content at 12 cm, 24 cm and 44 cm’s depth. This variation indicated that the cement mortar joints hold less water than the bricks.

The moisture content was 10 – 30% by volume in the old masonry wall, but below 10% in the more recent facing wall. The highest water content was 50 – 60 cm deep in the wall, where it almost reached saturation. One reason for the large difference was possibly that the hard fired bricks and cement mortar had a lower porosity and was less permeable than the lime mortar and soft fired bricks. Another reason was that the recent facing wall did not have sufficient contact to the old wall. Cavities at the interface would prevent the moisture from migrating from the old wall into the new.

The profiles indicated that the main source of moisture was rising damp, and that the source was quite abundant. The water level in the adjacent lake was approximately 2 meter below ground level. It is not exactly known how the wall foundation was made. Another possible source is dampness from the soil. Wind driven rain was not an important parameter, although west is the predominant wind direction in Denmark.

The moisture content was measured every two months for a year (fig. 5). There was a variation of 2 – 5% by weight, but no indication of a permanent change in water content. The repointing of the joints seemed not to have any immediate effect. Evaporation to the inside would be more effective, since this space is both heated and ventilated. But there was no benefit of the effort to control the interior climatic conditions. The source of water from below is possibly too abundant to be counterbalanced by evaporation.
Figure 2. Left side: Cross section of the wall with the position of the access tubes. Right side: Principal sketch of the moisture distribution over the cross section.

Figure 3. Exterior view of the cylindrical building at Frederiksborg Castle.
Figure 4. The initial moisture profile at 30 cm above ground (left) and 140 cm above ground level (right). Each profile was determined with a 1 cm interval between the readings.

Figure 5. The moisture profiles at 30 cm above ground (left) and 140 cm above ground level (right). Each profile was measured with a ten cm distance between the readings, five times over the year as indicated for each graph.
3.2 Garden wall at Marienlyst Palace
Marienlyst Palace and Garden is located in Elsinore in North Zealand. The present building date to 1760, but the garden and its perimeter wall is from the 15th century. The wall is made of red fired clay bricks and lime mortars joints, and is approximately 3.0 m tall and 45 cm thick. The terrain on the garden side is 1.5 m higher side than outside the wall. It has had a variety of surface treatments over time, last a cement render.

A pilot project was initiated to find the most appropriate solution for future restoration of the wall. A part of the program was to determine the distribution of moisture and to evaluate the effect of different renders on the moisture content of the wall. Three access tubes were installed at 0.4, 1.0 and 1.8 m above ground in each test area. The lower access tube extended 30 cm into the soil at the garden side of the wall. Some preliminary results from the reference area are given below.

The initial moisture profiles were determined with a distance of 1 cm between each measurement. The initial profile at 100 cm above ground level is shown in fig. 8 (left). The moisture content was 5 – 25 % by volume with a maximum towards the back side. The dip at 35 cm was due to a vertical joint parallel to the surface of the wall. The bonding of the masonry had an influence on the shape of the moisture profile. It is not possible to avoid the vertical joints when the access tubes are installed. Their influence must be taken into account when interpreting the measurements.

The moisture content was measured four times during a year (fig. 9). There was a gradual rise in water content at all three levels. The rise was uniform over the cross section, so it was not possible to identify the source of moisture for this change. Rising damp was not an important parameter, as the 40 cm profile had lower moisture content than the 100 cm profile. The wall has a stone foundation in a coarse sand deposit below the top soil. The ground water level was not identified, but any significant rising dampness in the sand layer would not be possible.

All three profiles had higher moisture content at 0-10 cm than at 10-20 cm. This implied an uptake of wind driven rain from the surface. The test areas were protected by a canopy, but this was not mounted over the reference area (fig. 7). The liquid uptake of the cement render was measured with a Karsten tube and found to be very slow. It is likely that the cement render repelled most of the wind driven rain. The salt content of the masonry was in general very low, but a moderate contamination of 0,1 % by weight of sodium chloride was identified at 0-10 cm. This was the reason for the apparent high moisture content at the surface.

The profiles indicated that the main source of moisture was the elevated terrain at the garden side of the wall. This would give a moisture distribution shown in fig. 6 (right side). The backfill soil held water content at 20 – 25 % by volume, but this did not penetrate into the wall at the low level. Perhaps the back side of the wall had a moisture membrane to protect the masonry against water migration. This will be further investigated by an excavation along the inside of the wall. A possible recommendation would be to protect the wall better against water migration from behind. If this intervention is not an option, the main challenge for a new render seems to be the water migration from behind.
Figure 6. Left side: Cross section of the wall with the position of the access tubes. Right side: Principal sketch of the initial moisture distribution over the cross section.

Figure 7. View of the garden wall from the outside. The reference test area is to the left.
Figure 8. The moisture profile at 100 cm above ground. Left: Initial profile measured with a 1 cm interval between the readings. Right: The evaluation over one year with 10 cm distance between the readings.

Figure 9. The moisture profiles at 40 cm above ground (left) and 180 cm above ground level (right). Each profile was measured with a ten cm distance between the readings, four times over the year as indicated for each graph.
4. Conclusion

The moisture distribution in two solid masonry walls was determined by the use of a dielectric probe. Horizontal access tubes with a diameter of 27 mm were permanently installed in different levels above ground. This allowed consecutive measurements of the moisture profiles in exactly the same positions every time. The profiles were much influenced by the material properties and the wall structure. Any difference in pore volume and water retention of bricks and mortar reflected in the moisture content. A salt contamination also had a decisive effect on the readings of the instrument. This must be taken into account when interpreting the results.

The initial moisture profiles were determined with a 1 cm interval between the individual readings. These profiles indicated the position of vertical joints or cavities. The evolution in water content was monitored in 10 cm intervals over a year. When combining the one-dimensional profiles it was possible to create a two-dimensional diagram of the moisture distribution over the cross section. The source of moisture to the wall was identified and the effect of future interventions could be monitored. This methodology is suitable for in-situ experiments, but the use is limited by the invasive nature. It is not appropriate or permissible to drill holes in any historic building or structure.

Acknowledgment

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References
"ELECTRO-PHYSICAL" METHODS TO STOP RISING DAMP.
ASSESSMENT OF THE EFFECTIVENESS IN TWO CASE STUDIES

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Abstract
Rising damp is a recurrent hazard to ancient buildings and its relevance is expected to increase in future, due to climate changes. In spite of the large diffusion of methods and products to stop rising damp, scientific literature on their effectiveness in the field is often scarce and not conclusive. This is particularly true for recent solutions; examples are the “electro-physical” methods, which are currently flourishing in many countries. These methods are often lacking a scientifically based proof of their working principles and effectiveness. Within the JPI-CH project EMERISDA, the effectiveness of two different commercial electro-physical devices was investigated in two case-studies. The devices were positioned in such a way as to include humid walls under the influence of the device as well as humid walls, comparable in orientation and structure, out of its reach, to be used as reference. The effectiveness of the devices was assessed by collection of samples at different heights and depths in the walls and gravimetric determination of their moisture content. Conclusions are drawn on the effectiveness of the methods by comparing the moisture content before and one year after the intervention, taking into account the variation in moisture content in the reference walls.

1. Introduction
Rising damp, i.e. capillary rise of water from the ground into a construction, is a well-known phenomenon in ancient buildings and one of the most recurrent hazards to monuments [1]. The phenomenon of rising damp is more common in old than in new masonry, as old buildings have often masonry foundations and lack of a damp-proof course, i.e. of a layer hindering the water transport from the ground to the upper structure.

The relevance of the rising damp problem is reflected by the large and varied offer of solutions present on the market, which, however, is not corresponding at all with the very limited available scientific information. Scientific research in the field on the effectiveness of methods
to tackle rising damp is limited by several factors: i) first of all, the long-term monitoring needed for a reliable evaluation of the interventions often leads to budget depletion before reaching a definitive assessment of the effectiveness of a method or product ii) besides, the combination of different interventions (e.g. chemical injection and special dehumidifying or salt resistant plasters etc.), common in the conservation practice, makes it arduous to point out the actual effectiveness of each of them.

The wide and differentiated offer, together with the scarcity and fragmentation of scientific and especially independent information on the different solutions, make it difficult, even for the professionals working in the field, to choose a suitable method on a sound basis. Choices of building owners are more often based on reliance on the promises of the producer than on scientific evidence of the effectiveness of the method.

In 2014 the research project EMERISDA [2] was set up, involving Belgium, Italy and The Netherlands with main aims: (i) coming to a scientifically based evaluation of the effectiveness of different methods against rising damp and (ii) defining a decision support tool for a conscious choice and successful use of these methods in the practice of conservation. Within this research, different types of interventions and products to tackle rising damp are investigated. In this paper, the results of the assessment of two different “electro-physical” methods are reported. Within “electro-physical methods” are included methods, which claim to be based on the use of electromagnetic waves, earth radiation or similar phenomena (see also [3]). Electro-osmosis is not included in this group.

In the recent years the application of these devices has considerably increased. Often these methods are applied on cultural heritage buildings, because of both their reversibility and their easiness of application and thus compatibility with historic fabrics, facts which favour the approval of the intervention by the conservation agencies. However, at the authors’ best knowledge, no scientific literature on the principles and effectiveness of these methods exist. The producers and sellers of these systems point at the positive experiences in practice, which up to now however have not been reproduced by independent scientists.

In this research we have assessed during a period of one year the effectiveness of two types of “electro-physical” devices, applied in two historic masonry buildings in the Netherlands. The assessment has been based on measurements of the moisture content (by gravimetric method) in the walls before and after about one year from the application.

2. Materials and methods

2.1 “Electro-physical” devices

The effect of two different types of electro-physical devices has been investigated in this research. Hereafter the properties of the devices are reported, as far as these could be defined on the basis of the information provided by the producer. Device A consists of a box which, connected to the electric power, should lead to a decrease of the moisture content in the wall thanks to an increased drying. The working principle is claimed to be a modification of the water molecule, which would affect the surface tension of water and thereby favour evaporation. Device B consists of a box which, connected to the electric power, should lead to
a decrease of the rising damp in the wall. In this case the working principle is not clearly described by the producer but simply defined as wireless electro-osmosis. Such a definition is obviously incorrect, as no electrodes are inserted, neither in the wall nor in the ground.

2.2 Case studies
The electro-physical devices have been applied on two historic buildings: the Paardenmarkt building in Delft (device A) and the St. Bavo church in Haarlem (device B).

The Paardenmarkt building complex is a Dutch national monument dating back to the 17th century. This monument consists of 2-floor masonry buildings around an inner court. One of the buildings was selected for testing (Figure 1). In this building damage, due to the combined presence of moisture and salts, is clearly visible in the lower part of the interior walls in the form of moist spots, peeling of the paint and scaling and crumbling of the plaster. This building was selected for different reasons: (i) the suspected presence of rising damp, suggested by the decay pattern and the high level of groundwater at the location; (ii) the possibility of carrying out extensive sampling; (iii) the fact that the building was not in use (and therefore the interior climatic conditions were not affected by heating and/or air conditioning); (iv) the long shape of the building which makes possible to keep some parts, out of the area of influence of the device, as reference.

Figure 1. Interior of the selected building of the Paardenmarkt in Delft (The Netherlands).

Two devices of type A were installed in April 2014. The location of the devices was decided by the producer of the device. It was chosen to use two devices, as the presence of metal beams present in the building might negatively influence the effectiveness of the device; in this way this risk is excluded. The area of influence of the device (according to the producer) with respect to the sampling locations are shown in Figure 2. Due to the anticipation of the restoration works, the devices had to be removed already in January 2015, earlier than originally planned.

St. Bavo’s church is one of the most important Dutch monuments (Figure 3). Dating back to the Middle Ages (construction started around 1400 [4]) the building consists of 3 naves, a transept and a choir with one apse. The interior brick masonry walls are plastered, with details in natural stone; the columns are, at least as far as visible, constructed in natural stone. The lower part of the columns and, to lesser extent, of the plastered wall, suffer of decay in the form of salt efflorescence and crypto-florescence, scaling and exfoliation of the natural stone and peeling of the paint layer. These damage patterns suggest the presence of rising damp. A device
of type B was installed in January 2015 at the location shown in Figure 4 and is still present in the church.

Figure 2. Plan of the Paardenmarkt with indication of the position of the devices, of their area of influence (circle) and of the sampling locations. Locations 1 and 4 are within the area of influence of the devices; locations 2 and 3 are outside and are thus considered as reference.

Figure 3. Interior of the St Bavo’s church in Haarlem (The Netherlands).

Figure 4. Plan of the St. Bavo’s church with indication of the position of the device, of its area of influence (circle) and of the sampling locations (all locations are on internal walls). Locations 1 and 2 are within the area of influence of the device; location 3 is outside and is thus considered as reference.
2.3 Investigation methodology

The effectiveness of the dehumidification devices to stop or mitigate rising damp has been assessed by comparing the moisture content in the wall before and after several months from the application of the devices. Samples have been taken from locations within and outside the area of influence of the dehumidification devices (Figures 2 and 4). The reference sampling locations allow to ascertain whether an eventual decrease in moisture content in the treated areas is due to a general decrease of the moisture content in the wall (as it can occur due to seasonal variations in the ground water level or in the amount of precipitation) or to an actual effect of the devices.

The moisture content has been assessed by drilling powder samples in the masonry at different depths and heights along vertical profiles and determining their moisture content gravimetrically, after drying the specimens in the oven at a temperature of 60°C. The moisture content (MC) is expressed as % of the dry weight of the sample and calculated as follows:

\[ MC = 100 \times \frac{\text{initial weight} - \text{dry weight}}{\text{dry weight}} \]  

Additionally, the hygroscopic moisture content of the samples at 20 °C 95% RH (HMC) has been measured by storing the samples in a climatic chamber under these conditions for a period of 4 weeks. The hygroscopic moisture content is expressed as % of the dry weight and calculated as follows:

\[ HMC = 100 \times \frac{\text{weight after 4 weeks at 20 °C 95% RH} - \text{dry weight}}{\text{dry weight}} \]

The HMC gives an indication of the presence of hygroscopic salts [5]; a MC higher than the HMC indicates that a moisture source, other than the moisture uptake given by the hygroscopicity of the salts, is present. A HMC higher than the MC and with the same distribution pattern through height and depth, suggests that the main moisture source is the hygroscopicity of the salts.

Because MC and HMC are expressed as weight %, samples should be collected as much as possible in the same material (brick or mortar) in order to facilitate their interpretation. In case materials with very different water absorption are present, the most absorbing material should be preferably sampled. In this case, as brick and mortar constituting the masonry have a quite similar absorption, it has been decided to collect samples in the brick. Besides, the plaster layer, when present, has been sampled separately. Care has been taken to collect, as far as possible, samples from the same brick unit before and after application of the dehumidification devices.

On selected samples, soluble salt concentration (anions and cations) has been quantified by ion chromatography (IC) carried out by Ion Chromatograph Dionex ICS-900 (Anions analysis: Column S23 Pre-column G23; Cations analysis: Column CS12 Pre-column CG12).
3. Results

3.1 Paardenmarkt
The moisture content (MC) distribution measured in the walls of the Paardenmarkt before the application of the dehumidification device of type A is reported in Figure 5. These results show that the MC in the lower part of the wall is high; the MC decreases with height and increases with depth and is generally higher than the HMC (Figure 5). These features confirm the presence of rising damp from the ground. At some locations (location 1, height 150 cm) additionally to rising damp, possibly also another moisture source, most probably rain penetration, may be present.

The HMC is locally high; this occurs mainly at the surface (plaster, 0-2 cm depth) and at the upper fringe of the rising damp, where evaporation occurs. The high HMC indicates that hygroscopic salts are present. Ion Chromatography (IC) analyses carried out on a selection of samples from location 3 (Figure 6), to assess the type of salts present in the masonry. The results show the presence of chlorides, nitrates and, at some spots, sulfates. Chlorides and nitrates are highly hygroscopic and explain the high HMC measured. Nitrates may come from the original use of the location as place for trading horses and cattle.

Six months after the application of the dehumidification system and immediately after its removal (10 months after its application) the moisture content of the wall was measured again.
Due to a problem in the power supply, one of the devices (device 1) did not work properly during the entire 10 months period. This might have altered the results at location 1. In Figure 7 the MC before and after 10 months after the application of the device is shown for all locations. For simplicity only the MC at the surface (0-2 cm) and in depth (5-20) is shown. At location 1 a slight decrease in MC is observed at all depths. However, no drying effect of the device is measured at location 4. Besides, at the reference location 3, a decrease in moisture content is measured as well. Similarly, neither significant increase in the HMC at the surface nor intensification of the severity of the decay (as might be expected by an enhanced drying and subsequent salt crystallization) has been assessed.

Figure 6. Ion content in samples from location 3 (Paardenmarkt building)

Figure 7. MC in the masonry walls of the Paardenmarkt before and after 10 months since the application of the humidification devices
3.2 St. Bavo’s church
The MC and HMC distribution before the application of the dehumidification device type B is reported in Figure 8. At location 1, the MC measured in the wall increases with depth and decreases with height, suggesting the presence of rising damp from the ground. It is striking to observe that the MC distribution at locations 1 and 2, at just a few meters distance from each other, is significantly different: at location 2 the MC is much lower. This might be related to differences in the material properties, a common fact in old masonry. At location 3 a high MC is measured in depth in the wall (15-30 cm) that decreases towards the surface. Also in this case rising damp from the ground is most probably present. The HMC is very high in the plaster all over the height of the wall; the highest values are measured at the height where the masonry dries and the salt accumulates. In spite of the very high HMC measured at location C, neither damage nor efflorescence are visible on the plaster.

The ion chromatography results (Figure 9) carried out on a selection of 4 plaster samples, helps to clarify this issue. The samples from location 3 (P33 and P41) contain a large amount of Ca++ and NO3-, which are likely combined to form calcium nitrate salts. Considering that the RH in the church is probably high (no heating is present), calcium nitrate can be assumed to be most of the time in solution. In fact, the deliquescence relative humidity of calcium nitrate in its

Figure 8. MC and HMC (weight %) in the masonry walls of the St. Bavo church before the application of the dehumidification device
highest hydrated form, Ca(NO₃)₂ · 4H₂O (nitrocalcite), is quite low (53.1%) [6]. Besides, lower hydrated forms of calcium nitrates have even lower RH of equilibrium, therefore hydration/dehydration transitions can hardly occur. These considerations can explain the absence of damage at these locations, in spite of the high HMC and high ion content measured in the samples.

The MC of the wall has been measured again after 1 year from the application of the dehumidification device. At location 1 the sampling had to take place about 70 cm right from the originally measured location, due to the placing of a tombstone against the wall at the location of the original sampling. The MC, before and after one year of application of the dehumidification device B, is reported in Figure 10. Also in this case no significant differences between location 1 and 2 (under the influence of the dehumidification device) and 3 (reference) are observed. At location 2, in depth and in the lower part of the wall, the MC has even increased.

Figure 9. Ion content in samples from locations 1 (P9, P13) and 3 (P33, P41) (St Bavo church)

Figure 10. Difference in MC in the masonry walls of the church of St. Bavo before and after 1 year from the application of the humidification device.
4. Discussion and conclusions

This research aimed at assessing, in the field, the effectiveness of dehumidification devices based on not better clarified “electro-physical” principles. As the working principle of these devices is not clearly defined and/or explained by the producers, research has been limited to assess whether, after one year from the application, any significant and consistent reduction of the moisture content in the walls occurs. To ensure objectivity to the research, the moisture content has been assessed gravimetrically, sampling before and after application has been carried out in the same season of the year and reference locations, outside the range of action of the devices, have been sampled as well.

Based on the results of this research, it is concluded that in the studied cases no significant and consistent reduction of the moisture content has been measured in the masonry of the Paardenmarkt building and St. Bavo’s church after respectively 10 and 12 months from the application of the devices. Over this period, no clear effectiveness of the devices is found.

It should be mentioned that, in spite of the care taken to ensure objectiveness to the study, assessment of the long term effectiveness in the practice is prone to several limits. This makes it very difficult to definitely assess, without any doubts, the effect of de-humidification methods through field studies (for example, the side conditions cannot be easily controlled and sampling is, for obvious reasons, restricted to a limited number of locations). In this research limits were given by: the forced stop of the research due to the anticipation of the restoration works in the case of Paardenmarkt, the not continuous functioning of the electric power, the change in the church interior which made it impossible to repeat the sampling exactly at the same location and the considerable difference in moisture content even between nearby locations, most probably due to differences in material properties and irregularities, as usual in old masonry. These considerations suggest that in order to definitely assess the effectiveness of dehumidification methods the combination of long-term experiments in laboratory, on scale models (built on purpose), and large scale monitoring of intervention in the field, is needed. We are working towards these objectives in the running JPI-CH project EMERISDA.

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RISK ASSESSMENT AND MITIGATION THROUGH
HYDROTHERMAL MODELING OF HISTORIC MASONRY

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Abstract
Rainwater migration through masonry walls is a recurrent concern for the restoration of cultural heritage, both at their exterior and interior surfaces, causing damage due to freeze-thaw action, salt crystallization, biological growth, staining, etc. Solving such problems requires an understanding of the migration of moisture throughout the masonry structure. Material characterization combined with computer modelling of the combined heat and moisture mass transport can assist to evaluate the actual state of conservation and possible restoration measures to mitigate the risks. Essential here to is the characterization of the material properties related to heat and moisture transport, especially the pore structure characteristics of the materials involved. The limits and possibilities of such an approach in practice are illustrated with two cases: the 18th century Saint Nicholas’ church of Aaigem and an Art Nouveau style residential house in south-east Antwerp developed around 1904. Both edifices exhibit damage related to rainwater migration at their west wall. However, structural differences and varying material properties required entirely different approaches to mitigate the problems caused by the rainwater penetration.

1. Introduction
Most of the damage phenomena encountered in cultural built heritage are related to the presence of moisture. Without moisture, damage phenomena such as frost, salt crystallisation or biological growth wouldn’t be a concern. Hence, our interest to understand how moisture migrates throughout and in between the porous materials that compose a masonry structure, especially where (wind driven) rain is concerned. Hydrothermal modelling of masonry structures, coupling heat, moisture and mass transport in porous building materials, can be a powerful tool to assist the risk assessment and mitigation of rainwater in historic masonry.
Dedicated material sampling and analysis serves as material characterisation for the modelling approach. These methods are illustrated with the results of two case-studies.

2. Methodology

The hydrothermal modelling of masonry structures is realised by means of the numerical simulation software Delphin (v5.6.9), developed at the T.U. Dresden for an analysis of the coupled heat, moisture and mass transport in porous building materials. The necessary material parameters for the hydrothermal modelling of the masonry composite are the density, the thermal conductivity coefficient, the capillary water absorption properties and the pore structure characteristics of the various materials involved. The material properties describing the capillary water absorption are the rate of capillary water absorption ($A_{cap}$, kg·m$^{-2}$·s$^{-0.5}$) and the total amount of capillary absorbed water ($w_{cap}$, m$^{-3}$·m$^{-3}$). These properties are obtained from a straightforward capillary absorption test [1].

As for the pore size characteristics, the total pore volume of a material and the pore size distribution are determined by mercury intrusion porosimetry (Micromeritics Autopore 9500 with a maximum attainable pressure of 30,000 psi). Where no capillary absorption measurements can be realised due to the restricted sizes of the samples lifted, the capillary absorption properties are estimated based on a comparison of their pore size distribution with mortar samples with comparable pore size distribution of which the capillary absorption properties are known from earlier studies. The density of the materials is derived from the mercury intrusion porosimetry, whereas the thermal conductivity coefficient is estimated from available literature [2].

The analysis of the presence and distribution of moisture and salts is determined gravimetrically and by ion chromatography (IC, Metrohm) as described in [3]. The in-situ water absorption of the facade is determined with the Karsten tube [4].

3. Case studies

3.1 Saint Nicholas’ church (Aaigem)

The Saint Nicholas’ church is an 18th century hall church with a 13th century gothic east tower (Fig. 1), situated in the small village of Aaigem. The church was restored some 20 years ago, including the removal of the lime wash and paint layers from the western and northern facades. Since then, the western facade has never been without problems: paint layers peel off, biological growth is evident while moisture and salts cause damage to the interior. Over the past years the west facade has been painted over several times, however without solving any of the problems.

Today the problems are mainly visible from a height of approximately 6 m on the western facade, both at the interior and exterior. Two core drillings were lifted, one from the bottom of the wall (at ca. 1 m height) and one within the severely damaged area (at ca. 8 m height), to analyse the structural built-up of the exterior walls and to sample materials for laboratory analyses. In addition, powder drilled samples were lifted from the interior to determine the
presence and distribution of salts in the depth and in-situ absorption measurements were carried out on the exterior facade to study the water absorption on the paint layers.

Both core drillings fell apart completely, evidencing multiple fractures across the mortar joints and within the bricks. Within the damaged area, the core drilling revealed a triple leaf wall with 10 cm brickwork on the outside, some 40 cm of natural stone on the inside, from the Lede formation, and about 30 cm of loose conglomerate in between, which fell apart entirely while drilling and mainly ended up washed away. The core drilling at the bottom of the wall consisted of some 50 cm of brickwork at the exterior facade, also broken into numerous pieces, and a 20 cm thick inner facing of natural stone of the same formation as above.

From the cores different samples were selected from the brick, the natural stone and the bedding mortar to characterise their physical properties (Tab. 1). Because of the cores’ fragmentation, the amount of samples which could be selected for analysis was limited. For the brick for instance, the rate of absorption and drying could only be determined on 2 samples, which revealed more or less comparable results. The rate of capillary absorption of the brick is about 65% higher compared to the mortar and also higher than both fragments from the natural stone. The pore size distribution of the bricks is characterised by a distinct maximum pore diameter between 5 and 8 μm, with a decreasing amount of finer pores up to approximately 1 μm in diameter. Some brick fragments possess a small amount of smaller pores in the range of 0.2 to 0.3 μm in diameter, which could increase the amount of water being held within the pores.

The two fragments of the natural stone are characterised by distinctly different water absorption properties (Tab. 1). Visually a clear distinction is observed with the natural stone from the core drilled at the onset of the vault (higher up the wall) being more compact compared to the stone found at the bottom of the wall. The more dense stone above is
characterised by a much slower capillary water uptake and a lower saturation moisture volume. Not only its rate of water absorption is low, also the drying of the compact limestone proceeds at a reduced velocity. These different properties are reflected within their pore size distribution. The pore size distribution of the more dense stone is characterised by pores with much dispersed pore diameters, ranging from the smallest of pores to macropores, however with the majority of them comprised between approximately 80 nm and 0.7 μm in diameter. The total porosity of the stone fragment is also low, all of which explains the slow capillary uptake and the low amount of water being absorbed by capillarity. The other stone fragment is more porous and has mainly larger pores with a distinct maximum around 8-10 μm in diameter.

Table 1: Overview of the density (ρ), the capillary water absorption coefficient (A_cap), the total amount of capillary absorbed water (w_cap), the total accessible pore volume (Φ₀) and the median pore size by volume (d_median) of the brick, natural stone and mortar sampled from the core drillings. The averaged data are represented with the standard deviation in between brackets, if more than one measurement was obtained.

| Material    | ρ (kg/dm³) | A_cap (kg·m⁻²·s⁻⁰.⁵) | w_cap (kg·m⁻³) | Φ₀ (vol.% | d_median (μm)
<table>
<thead>
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<tbody>
<tr>
<td>Brick</td>
<td>1.660 (0.110)</td>
<td>0.5668 (0.0566)</td>
<td>175.5 (26.1)</td>
<td>29.7 (3.5)</td>
<td>5.9 (2.3)</td>
</tr>
<tr>
<td>Natural stone</td>
<td>2.418 (0.023)</td>
<td>0.0113 (0.0172)</td>
<td>52.9 (19.3)</td>
<td>9.4 (0.7)</td>
<td>0.6 (0.1)</td>
</tr>
<tr>
<td>Mortar</td>
<td>1.359 (0.093)</td>
<td>0.3427 (0.0483)</td>
<td>388.3 (23.2)</td>
<td>43.9 (2.5)</td>
<td>0.2 (0.1)</td>
</tr>
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Petrographic analysis reveals that the masonry is constructed with a hydraulic lime mortar with very fine quartz sand. The maximum grain size of the sand is estimated at only 0.16 mm. Based on chemical analysis, the mortar composition is estimated at some 3 to 4 volumes of lime per volume of sand. It creates a very dense mortar matrix with mainly smaller pores in diameter ranging from a few nm to a few μm. The main corpus of the pore sizes can be situated between 50 nm and 1 μm, explaining its lower capillary absorption coefficient in comparison with the brick and certainly the high amount of capillary absorbed water. Almost every pore within the mortar will attribute to the capillary water absorption. Despite the fact that the mortar contains mainly smaller pores, its total porosity is very high.

As for the exterior surface the water absorption is negligible. The paint layers, which are waterproof, prevent rainwater from being absorbed by the masonry and therefore also slow down the drying of areas wetted through cracks. Although the paint layers are only a few years old, various haircracks are present which enable wind driven rain to enter the masonry. Naturally, areas where biological growth or possibly frost action have damaged the paint layers are preferred places where rainwater will be absorbed by the substrate. The analysis of
the presence and distribution of moisture and salts at the interior face of the western facade proves that moisture is omnipresent within the brick, mortar and plaster. Salts other than gypsum are however only found within the plaster. In the substrate no traces of salts excluding gypsum appear, hence it is assumed that the salts were introduced with the plastering and are easily removed once the severely damaged plaster is replaced.

Modelling the complete hydrothermal behaviour of such a complex and heavily fragmented masonry is not feasible. The main objective of the approach here is to understand how moisture will migrate through the entire structure and to focus on the possibilities for protecting the substrate from getting wet, while enhancing drying in the case the substrate got moistened.

Evaluation of the hydrothermal behaviour of the masonry evidences that the bedding mortar transports the rainwater through the entire wall. Any water passing through the paint layers at the exterior surface is easily absorbed by the brick, which than passes it on to the bedding mortar. Also close to the surface the amount of water absorbed by the brick never exceeds 20% of its capillary saturation. Hence, the risks for direct frost damage to the brick are almost neglectable. As the amount of moisture in the bedding mortar increases it slowly migrates deeper within the wall. Through a continuous bed joint rainwater will easily migrate to the inner surface of the wall. Furthermore, an internal vertical cut through the bed joint of the dense limestone or brick will not prevent the moisture from attaining the inner surface of the wall. If the presence of the paint layers at the exterior is removed, drying will only influence the outer parts of the wall. At the inside of the wall the bedding mortar will always be moist, facilitating rainwater penetration once a new rain shower occurs. Rainwater migration to the interior finishes is mainly a concern on the western facade, however, due to the structural complexity of the wall moisture appears to be forced through the wall preferentially causing damage locally on the inside.

Mitigating rainwater penetration on the western facade of the church is practically impossible. With the materials, brick and bedding mortar, present at the external surface only a hydrophobic finish will be able to prevent rain from being absorbed by the substrate. However, the possibility of rainwater penetration through (hair)cracks, if not present immediately, they may appear with ageing. When considering a hydrophobic finish defects should always be considered. In such a case, the hydrothermal modelling evidences that the water vapour permeability has a decisive influence on the possibility for the substrate to dry out. Even an increase of the water vapour retarding factor ($\mu$) from 5 up to 20, will result in a strongly reduced drying of the substrate (Fig. 2).

The best approach to mitigate the problem of rainwater migration is therefore to apply a lime wash with a reduced rate of capillary absorption ($< 0.05 \text{ kg m}^{-2} \text{s}^{-0.5}$). For such a finish, the influence of the water vapour permeability will only determine the drying rate of the substrate at $\mu$-values above 2000, while the rate and amount of water absorbed by the substrate is reduced. Although this approach will reduce the amount of rainwater absorbed at the external surface, it will not prevent moisture from attaining the inside of the wall under the most severe conditions. Therefore, additional care should be taken to replace the plastering with a lime plaster and a vapour permeable finish ($\varphi$-value below 0.05) in order for the finished
plaster to let the wall dry out easily. Any problem related to salts is mitigated as soon as the existing plastering is taken off.

![Figure 2](image)

Figure 2. Evolution of the moisture content (m³·m⁻³) in the brick and bedding mortar as function of the material characteristics (capillary water absorption coefficient $A_{cap}$ (kg·m⁻²·s⁻⁰·⁵) and water vapour retarding factor $\mu$, see legend) of the lime wash upon drying from an initial average moisture content of 0.15 m³·m⁻³. Drying of the wall is simulated under true external climate conditions (temperature, relative humidity, sun and wind), excluding however the influence of rain.

3.2 Residential house ‘De Violier’ (Antwerp)
The residential house ‘De Violier’, named after the flower *Matthiola incana*, was constructed around 1904 by architect Jules Hofman in art nouveau style (Fig. 3) and is characteristic to the south-eastern quarter of Antwerp where the house is situated. A recurrent problem is rainwater penetration through the westerly oriented front facade, which is constructed with a yellow face brick and elements in French limestone (Savonnières and Euville). Various interventions have so far not been able to solve the issue of rainwater penetration, causing severe damage to the inner plastering and paintworks. The damage is more pronounced at the higher floors as, within the urban landscape and the quite narrow streets, the top of the house will be more influenced by wind driven rain. In the past 20 years the front facade has been repointed and at least twice been treated with a water repellent, to no avail.

The yellow toned brick at the outer surface is a hollow brick, which does not continue through to the inner face of the wall, where a common porous red brick is found. The thickness of the wall varies as part of the artistic style. Adjacent to the windows the total wall thickness is only one brick, almost immediately thickening to 1.5 brick and to 2 bricks even further away. For the brickwork, both at the external and internal surfaces, an almost black bedding mortar has been used. At the external surface a cement pointing can be recognised, which is applied at a strongly varying depth albeit always more than 1 cm.
The structural built-up of the interior finish is quite complex, evidencing multiple interventions over the years. The interior finish was sampled at two locations in adjacent rooms on the second floor, where the damage due to rainwater penetration was most severe. The interior finish consists of alternating layers of dark grey, probably cement based, layers and white coloured, gypsum based, layers, all with varying thickness. Somewhere in between these layers, in both rooms, a beige tinted lime or loam plaster coat containing straw fragments was found as well.

At the moment of sampling, the bedding mortar (sampled from the exterior and interior faces) and the second white layer (near to the top) from the interior plastering were found to be very humid, containing between 7.0 and 18.1 wt.% of moisture.

The dark coloured, almost black bedding mortar was found to be presumably a slightly hydraulic lime mortar with a fine sand (maximum grain size below 0.34 mm) and the addition of a coarsely grinded slag (grain size up to 4 mm in diameter). The pronounced darkening of the mortar by the addition of slag is deepened further by the (deliberate?) addition of coal fragments (< 2 mm in size). The specific composition renders the mortar a pore size distribution with almost equally distributed pores ranging from a few nanometers up to
approximately 10 μm in diameter. Especially the very fine pores (smaller than 20 to 30 nm) distinguish the bedding mortar from all of the other materials found in the wall. The evaluation of the water absorption at the facade and the possibility for it to migrate to the interior surface was evaluated by in-situ measurements and laboratory analyses on sampled material from the bricks and mortars. While for the face brick, large enough samples could be lifted to allow for the capillary absorption to be obtained experimentally. The samples lifted from the internal brick, the bedding and pointing mortars as well as the plaster layers allowed only for their identification and the evaluation of their pore size distribution. The evaluation of the water absorption at the facade included in-situ measurements to evaluate the performance of the water repellent treatment(s) on the brick and natural stone, as well as to study the influence of (hair)cracks at their surfaces or in between the bricks and mortar joints on the water absorption.

The capillary water absorption tests on the yellow face bricks evidenced no significant differences in water uptake in between the external, side or internal (in contact with the perforation) surfaces. Water is absorbed slowly by the brick. The coefficient of capillary water absorption is determined at 0.044 ± 0.010 kg·m⁻²·s⁻⁰·⁵. However, the in-situ Karsten tube measurements evidence that the water uptake at the external surface of the brick is close to nil. At maximum 0.25 ml is absorbed over a period of 15 minutes in the Karsten measurement, revealing an upper limit of 0.026 kg·m⁻²·s⁻⁰·⁵. Furthermore, a capillary absorption test by means of dyed water on one of the lifted yellow brick samples evidenced that the outer surface, up to a depth of 0.5 to 1.5 mm, is not absorbing water. Hence, although the water repellent treatment is still sufficiently efficient at the surface, the water repellent, said to be applied at least twice over the past 10 years, only penetrated the extreme outer surface of the brick.

The water repellent treatment had its effect on the pointing mortar as well. A drop of water remains on the mortar’s surface for a few minutes before finally being absorbed. However, in-situ Karsten tube measurements on the mortar joints demonstrate that rainwater is absorbed rapidly into the substrate despite the water repellent effect on the brick surface and mortar joints. Hence wind driven rain will have a significant wetting effect on the exterior wall as rainwater enters the structure through (hair)cracks in the mortar joint or at the brick-mortar interface. As for the different mortars and the red brick at the inner surface of the wall no capillary absorption measurement could be realised due to the restricted sizes of the samples lifted. Their capillary absorption properties were estimated from earlier studies.

For the modelling of the water absorption at the surface an abstraction is made of the superficial water repellent treatment and the presence of cracks. Their influence on the hydrothermal behaviour of the structure is evaluated by sound reasoning with respect to the observations made in-situ. Although the original surface of the face brick and pointing mortar absorb water slowly any amount of water being absorbed will disappear in the bedding mortar as soon as its reaches the necessary depth. As with each rain shower the amount of water comprised within the bedding mortar increases and gradually migrates from the outer surface inwards, the interior brick and the first layer of the plastering become wet as well (Fig. 4). When the wall dries out, the water recedes in reverse order with the latter materials drying out first. The bedding mortar itself dries out close to both surfaces of the wall, however, within the wall it will remain wet as the intermittent drying periods are too short to realise a
The moisture distribution, as derived from the modelling, seems to correlate with the in-situ moisture measurements at the exterior and interior surfaces.

Figure 4. Distribution of the moisture (m³·m⁻³, see legend) within the front façade after 75 days (with the modelling started at January 1st 2000). The exterior surface is situated at the left side of the graph. The face brick and pointing mortar are both dry (white to light grey), which is also the case for the two outermost layers of plaster (right side). The bedding mortar, evidencing a moisture gradient from the exterior inward, the interior brick and the layer of plaster in direct contact with it are all wet (dark grey to black).

The model is restricted in its representation of the real hydrothermal behaviour of the wall as i) the superficial influence of the water repellent treatment on the mortar and brick is not considered and ii) the occurrence of (hair)cracks at the outer surface is not modelled either. Although the water repellent treatment will reduce or more probably impede water absorption at the materials’ surfaces, the presence of small cracks, as observed in-situ, will allow for wind driven rain to enter the wall easily, hence, attaining the bedding mortar straight away as modelled. Hence, it is most likely that the bedding mortar will be moist throughout the year and that right after periods of intense rain showers moisture will easily migrate through the bedding mortar to the interior finish.

The water repellent treatment on the face bricks is irreversible. However, even if the removal thereof would be possible, it wouldn’t solve the problem of rainwater infiltration as illustrated by the modelling, which actually describes the original hydrothermal behaviour of the walls. Repairing the mortar joints will, if the appropriate mortar composition is selected and carefully applied, eliminate the cracks at the surface and, hence, reduce the amount of rainwater being absorbed. However, in general it will not prevent from rainwater reaching the bedding mortar, except if a water repellent mortar joint is selected. The application of a traditional, capillary absorbent, lime or even cement mortar will increase the amount of water absorbed by the bedding mortar, but will, however, hardly increase the drying rate of the bedding mortar afterwards. In contact with the bedding mortar, the finer pores of the bedding mortar will always retain the water from being capillary absorbed by the new mortar joint. Hence, drying of the wall through the mortar joint will, whether the mortar joint is hydrophobic or not, always be defined by water vapour migration rather than pore water being evacuated to the external surface by capillarity. Nevertheless it’s most likely and should certainly be assumed that new cracks will develop reintroducing the problem of water infiltration. Hence the necessary actions should be taken to, temporarily, mitigate moisture from damaging the interior finishes. For this reason it is advised to replace the damaged plasters by a hydrophobic lime plaster with an appropriate finishing layer. Together with a
regular inspection of the external surfaces for new cracks to appear, such an intervention should prevent further moisture damage to the interior. In addition, the modelling evidences that the current problem is not a consequence of the more recent interventions. The problem of rainwater penetration was already present from the beginning, as the model closely resembles the original structure (with exception of the mortar joint). The built-up of the interior plaster in a series of very different layers is presumably also a witness of an historic problem of rainwater penetration.

4. Conclusion

The two case studies illustrate that hydrothermal modelling can be a powerful tool to analyse the damage processes and to evaluate various alternatives to mitigate damage, despite the difficulty to sometimes incorporate the true complexity of reality as the available hardware and calculation time require choices to be made to reduce the complexity of the computer model. Often the structural heterogeneity, the natural variation of material properties and/or the occurrence of thin or large cracks or voids within a material or on their boundaries need to a certain level be disregarded, although they may have a pronounced influence on the hydrothermal behaviour of the masonry composite. However, sound reasoning can often deal with such shortcomings of the computer models.

A recurrent problem is the occurrence of a bedding mortar with very fine pores, often in the nanometre range, due to the abundant use of putty lime or hydraulic lime as a binder, which will facilitate the inward migration of moisture from the external surface. Any mortar added as a pointing will always allow for moisture exchange in favour of the bedding mortar. Upon drying, capillary transport to the surfaces of the wall will always stall at a certain moment leaving the bedding mortar at the inside of the wall to dry out slowly by vapour transport through the already dried exterior surfaces. As a consequence, the bedding mortar will always be wet whatever solution is selected for repair of the external or internal faces of the wall. The application of hydrophobic mortars at the joint or as a plaster can either diminish the amount of water being absorbed at the external surface or prevent moisture from damaging the interior finishes. However, such a decision must always be evaluated case by case as it halts moisture (and salt) migration at a certain depth within the structure.

References

USE OF LOCAL STONE: CAUTIONARY TALES

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Abstract
Until relatively recently, locally available stone was used almost exclusively in construction, due to availability, limited transportation options and economics. Historically, naturally formed field stone was used for foundations, localized cladding features and in some instances entire building facades. Stone, perhaps more than any other natural building material, has numerous varieties and characteristics within its broader classifications. Many of these local stones were not necessarily appropriate for some applications and environmental conditions. Since around 1880, and continuing for perhaps 40 years, as quarrying techniques mechanized, the use of some local stones in larger and thinner individual units as cladding in multi-wythe exterior wall systems were replacing traditional monolithic field stone wall systems. As these “newer” wall systems have aged, these applications introduced challenges including unanticipated weathering characteristics, residual stresses and detrimental inclusions. Where and how these unique local stones are installed as well as climate and weathering patterns certainly contribute to the potential deterioration and serviceability challenges. This paper will focus on three stones used in the United States between the 1850s and the 1960s that have variable performances in various applications.

1. Introduction

Stone has been used as a building material for thousands of years. Its aesthetics and sense of permanence have made it a popular material, especially among builders and architects. Many of the significant buildings throughout history have been constructed of stone. Early stone monuments constructed of non-local material have been the source of numerous theories regarding how this material was transported over great distances. In reality, the method of extracting and transporting may be as simple as basic physics, in combination with inexpensive and available labor and the expectation that construction can be a generational endeavour, rather
than the highly accelerated pace required in today’s economic climate. The days of monumental royal constructions are mostly long over, but the desire to construct buildings using stone remains universal. The evolution of stone clad buildings closely parallels the evolution of building construction and technologies. Monolithic wall assemblies were the standard for thousands of years. Modern construction techniques attempt to minimize the amount of stone used to maintain the aesthetics a particular stone provides, to save weight and money. This change is a result of the evolution of structural and manufacturing technology allowing stone to be used and quarried in thinner applications than had historically been feasible. Historic quarrying and fabrication techniques relied on both local labor forces, local stone sources and basic transportation systems.

Historically stone was used for both decorative and functional purposes. With few exceptions, building systems incorporate inexpensive backup materials in combination with more expensive facing. Early stone structures were typically solid, multi-wythe, load bearing assemblies combining high quality facing stone finished to very tight tolerances with a looser rubble or brick backup. Once again, economics was critical to the development of exterior enclosure systems.

The Industrial Revolution of the mid-19th Century dramatically changed the building industry. Economics certainly still was the primary driving factor in almost all building construction, but mechanization provided advancements in the construction industry from machines to transportation. This resulted in the wider use of stone since it was now more economical in some respects. Transportation remained a major factor in the selection and use of stone throughout the world.

2. Stone Classifications

Unlike manufactured materials used in construction, the physical and aesthetic characteristics of stone vary greatly between geologically different stones as well as between stones of the same type. There are three types of stone, as defined by the process in which the way the stone is formed. Each type of stone has its own unique characteristics both aesthetically and physically. Sedimentary stones include limestone, sandstone, brownstone and shale. This type of stone is the product of deposits of sediment materials in prehistoric river and lake beds. Distinct bedding planes between individual layers of material and grain size characterize sedimentary stone. These inclusions present challenges depending on the application and exposure. Of the three classifications, these stones tend to be relatively soft, easy to carve, porous and absorptive. Igneous stones include granite and schist. This type of stone is the result of volcanic activity and the consolidation of molten magma. Classifications of igneous rocks are based on the silica content within the stone. These stones tend to be hard and non-absorptive. Finally, metamorphic stones include marble and slate. Metamorphic stones are the result of sedimentary or igneous stone being subjected to millions of years of heat and pressure resulting in a recrystallization of pre-existing rock. Two types of metamorphic processes can occur to change rock. The first is thermal where rock is subjected to prolonged exposure to heat in a confined environment. The second process is regional metamorphism and is associated with the creation of mountains where rock is subject to extended periods of stress or pressure.
During this process the recrystalization of the stone results in new rock particles forming parallel to the pressure. Metamorphic rocks are categorized based on the pre-metamorphosed rock. The physical and aesthetic characteristics of these stones can greatly vary.

3. Stone in Construction in the Midwestern United States

In the Midwestern United States large stores of limestone exist. Beginning in the 1850s, the use of locally quarried limestone for civil structures and building foundations became common. The stone was readily available and the physical properties were found to be desirable for civil and foundation applications. In these applications, the stone was quarried in relatively large blocks and installed with the bedding planes oriented parallel to the ground (naturally oriented).

Unlike foundations, when some of these sedimentary stones were used for cladding, the geological composition of the stone became more critical to the durability and workability and therefore appropriateness of the applications. As a cladding, the desire to use the stone in less natural applications was greater, thus resulting in situations with higher exposure and less redundancy in the material. Workability with respect to carving, and the desire for larger units used in alternate aesthetics to random coursing, began to expose the limited durability of some of the stone.

4. Case Study Stones

This paper will focus on three commonly used stones in the Midwestern region of the United States between 1850 and 1960 including Land Superior Sandstone, Kosota Limestone and Serpentine “Marble”. Each of these stones had a period of great popularity inevitably followed by a period where they fell out of favor. Use of these stones as an exterior cladding has all but stopped, but many examples remain and provide interesting insight into the issues which lead to their decline in use.

4.1 Lake Superior Sandstone

Lake Superior sandstones, generally classified as ferruginous sandstones [1], compositionally vary depending on the specific formation of the region, but generally are composed of quartz cemented with iron oxide, calcite, authigenic quartz or silica [2]. The cementing in this stone consist primarily of silica and iron oxide and generally determine the color of the stone [3].

Lake Superior sandstone was first used as a building material in the Midwest beginning in the 1850s. At the time, Lake Superior sandstone was touted to resist the detrimental effects of fire when compared with other contemporary stones. As a result, it gained great popularity as a durable, fireproof, decorative and coveted building material.

Prestige and regard for Lake Superior sandstone were also gained through the opinions of architects in Minneapolis, Detroit, Chicago and Cleveland on the value of Lake Superior sandstone. Lake Superior sandstone was made more readily available through the canal system.
and more so with the introduction of the Chicago, St. Paul Minneapolis, and Omaha Railroad in 1883 [4].

Deterioration of the sandstone has been an ongoing issue with many buildings in these areas (Figure 1). Ongoing deterioration is the result of prolonged exposure to rain and erosion of the binders between the sand particles. Deterioration mechanisms are further exacerbated by the physical characteristics of Lake Superior sandstone, such as shale and clay within some of the bedding planes, as well as susceptibility of face bedded units to rapid failure.

![Figure 1. Deterioration of Lake Superior Sandstone](image)

4.2 Kosota Limestone

Mankato-Kasota Limestone, otherwise known as Kasota limestone is a sedimentary rock that is quarried from the Oneota Dolostone formation located in southern Minnesota. The stone is quarried near the town of Mankato, Minnesota. Kosota limestone was used by Frank Lloyd Wright and several other well-known architects on many buildings in the Midwestern United States. The stone was generally used as accent. Recently the stone has become much less plentiful which has resulted in lower quality material. The rock is a very fine-grained dolostone consisting almost entirely of dolomite. The high dolomite content results in a relatively durable stone that for a period of time was widely used in buildings. Dolomite refers to stone principally composed of magnesium calcium carbonate compared to a true limestone that is principally composed of calcium carbonate. This particular stone is commercially referred to as Mankato-Kasota Stone after the location of several quarries. Dolomites are frequently grouped together with limestone because both of these are in the carbonate family.
Kasota limestone is characteristic of a medium high to high density limestone with very low water absorption (porosity). Based on the gross characteristics of the Kasota stone, the stone is relatively durable provided it is installed with the bedding planes properly orientated, and is allowed to fully dry prior to installation, and then installed properly. However, as local sources became depleted stone units with more clay within the bedding planes became a common problem. George P. Merrill explains the decay mechanism involved in Trenton limestone containing clay inclusions in this book, but the mechanism of deterioration holds true for any building stone containing clay bedding planes;

“These consist of alternating clayey and calcareous portions, the latter constituting the hard and enduring part of the stone. These layers are not always distinct and continuous over large surfaces, but the blend or shade into each other every few inches. Yet in the process of time, under natural weathering, they get separated so as to fall apart, the clayey material disintegrating first and causing the calcareous structure which sustains the whole to break up into small sheets or fragments.”

The clay particles will expand and contract from repeated wetting and drying of the stone. This expansion and contraction can create internal stresses within the stone similar to repeating freezing and thawing of water. Depending on the quantity of the clay particles, the internal stresses created by the wetting and drying of the clay can lead to shearing of the bedding planes, spalling and significant deterioration of the stone (Figure 2).

Water has long been associated with deterioration processes affecting masonry materials. Its presence within the interior pore structure of masonry can result in physical destruction if the
material undergoes wet/dry or freeze thaw cycling. The latter is particularly damaging if the masonry material has a high clay mineral content. Rock in the ground that is below the water table will be saturated with water. Since the rock has been in this condition for a prolonged period of time, the stone and the water are in equilibrium and any soluble components in the rock will be in the water. When the rock is extracted as a large block from the quarry it is no longer in equilibrium and pore water that contains soluble components will migrate to the surface during drying. Any soluble components will be left behind which results in case hardening of the stone particularly if the soluble components are deposited epitaxially. Quarry water or sap can be problematic if the water is trapped within the voids following initial quarrying. The latent water in stone will evaporate over a period of 1 to 2 years. As a result, limestone and sandstone are generally allowed to “dry out” for a period up to 2 years following quarrying prior to being cut for specific installations. A dense stone like Kasota limestone would be expected to dry out slowly.

4.3 Verde Antique

Verde Antique while having the “look” of marble is actually a "serpentine" and classified as a hydrous magnesium silicate [5]. With the hardness and durability of most granite, and its low absorption rate and high flexural strength, was an excellent choice for both interior and exterior uses. However, the variability and extensive veins of this stone produces widely varied test results. Failure typically occurs at the veins and rifts in the stone. Therefore in thicker applications the issue is of less significance.
Serpentine is a major rock forming mineral and is found as a constituent in many metamorphic and weathered igneous rocks. Serpentine’s structure is composed of layers of silicate tetrahedrons linked into sheets; this structure is what gives Verde Antique its high flexural strength rating.

Verde Antique is the commercial name for the serpentine “marble” derived from highly sheared ultramafic rocks that have been rewelded and metasomatized by the process of serpentinization. These ultramafic bodies are now recognized as segments of ancient oceanic crust that became part of the eastern North American continent during the Taconian orogeny. This is considered to be middle Ordovician in age, around 450 million years ago.

More deformation and metamorphism took place during the Acadian orogeny around 360 million years ago. This may have resulted in the polishable Verde Antique serpentine. While serpentines have been used to clad entire buildings, generally the use of the stone is limited to areas near grade where the character of the stone can be appreciated. This includes vestibules, storefronts and decorative spandrels. The veining, that provides the character defining features of the stone, is also typically the weakness. Similar to other highly veined marbles, fiberglass reinforcement is often applied to the back of the panels in contemporary applications. These are effective to a point, but if the veins are discontinuous even reinforcing will not be adequate since the stone is essentially cracked. In exterior applications the stone is very susceptible to atmospheric pollution, specifically SO$_4$. In exterior applications, the stone will readily lose a polished finish and the surface will become rough with deposits of talc and gypsum, which in turn react with water and in some instances efflorescence will develop from the magnesium.

5. Causes of Deterioration

All stone is susceptible to deterioration from various mechanisms including: moisture shedding characteristics, lack of proper maintenance, organic growth, inappropriate previous repairs, and inappropriate cleaning techniques. Freeze-thaw durability has long been known as a source of stone deterioration and a significant issue in the Midwestern United States [7]. In the case of sandstone and dolomitic limestones, clay laden bedding planes are far more susceptible to freeze-thaw deterioration than oolitic limestone as the clay will readily absorb water [8]. Most importantly, relative to the stone types described above a general vulnerability of the materials is based on application. This issue is further exacerbated when the stone is installed in a face-bedded orientation. Face-bedding is an economic-driven fabrication method that is commonly used when the proportions of the stone are greater in elevation than in plan. This creates a greater potential for face spalling and exfoliation of units when exposed to temperate weathering patterns, as the bedding planes are oriented perpendicular in the wall, to their natural orientation [9]. While the stones presented above provided an economical solution for particular application in localized areas of the Midwestern United States, time has provided the best indication that there are potential durability issues when using these local stones in many severe climates.
6. Repair Approaches

While it is often desirable from a preservation philosophy perspective to replace as little deteriorated stone with the same stone as necessary, yet in some instances this is not practical or appropriate. Often, the stone is no longer available and for good reason. Replacing severely deteriorated units or facade elements with an alternate stone in most instances is the accepted approach. In the case of the stones presented in this paper, a stone that is often substituted for Lake Superior Sandstone is St. Bees stone from England. The stone contains a similar red color, but is a bit bluer visually. A common replacement stone for Kosota limestone is known as Lannon stone. First quarried in the 1830s, Lannon stone was used throughout the Midwestern United States. The stone a dolomitic limestone quarried in southeast Wisconsin and is part of the Niagara Escarpment from the Silurian Period [10]. The stone is generally a gray to cream color and is quarried close to the surface and has excellent durability and very low absorption. This stone has been found to blend well with Kosota limestone. Unfortunately there really is not good replacement stone for Verde Antique. The stone remains available, but other means/stabilization and strengthening methods are necessary to install the stone in exterior applications.

As with any building facade repair project, developing an appropriate repair approach is a multi-faceted process. A typical investigation should include a review of available documents related to the facade including drawings, maintenance records and previous reports, a thorough inspection, an investigation of concealed conditions and field and laboratory testing of the constituent facade components including the stone and mortar. Based on the findings of the investigation, appropriate repairs, scope and prioritized phasing can be developed. These repairs may principally include stone replacement, but in addition consideration of envelope water management provisions, including roof drainage, repointing and crack repair are often necessary. Finally, appropriate cleaning and biogrowth treatment often helps to mitigate accelerated deterioration, yet in the case of stone with clay inclusions cleaning could cause further deterioration. Other repairs that are sometimes considered include patching, application of consolidants, pinning and re-sculpting of weathered elements. Each of these need to be approached with great care. Often times these techniques are ineffective at best and in some instances detrimental by accelerating the deterioration of the adjacent stone.

7. Testing

Historically, limited stone testing was performed relative to the appropriateness of a particular stone’s use in a particular climate [11]. This was not a significant issue when stone was used in large blocks in load bearing conditions. As stone applications became thinner, the need to understand the durability and mechanical properties of a particular stone became more critical. Compression strength, flexural strength, absorption and strength loss due to exposure and weathering need to be better understood with thinner applications. With the exception of compression strength and absorption, limited data of flexural strength and durability were historically available.
Petrographic evaluation should be used to evaluate stone in an effort to identify the mineral composition and structure of a stone. These findings in combination with past knowledge of those characteristics of a particular stone are helpful in predicting future performance. Mineral size and interlocking, as well as the presence of flaws or veins all contribute the durability. Another method of evaluation is to expose samples of stone to an accelerated weathering procedure, and evaluate the stones’ physical and mechanical properties for changes. Numerous testing programs have been conducted in the past 20 years that show that the strength loss of stone exposed to a specific accelerated weathering regimen correlates favourably to strength loss observed for that stone when exposed to real time in service weathering. The laboratory accelerated weathering regimen that has been found to be predictive of in service deterioration includes the following: submersion of flexural strength test prisms, 1/4 inch (6.3mm) to 3/8 inch (9.5 mm) deep, in a 4 pH sulfurous acid solution, to simulate acid rain. Specimens are subjected to 100 cycles of heating and cooling between -10° F to 170° F (-23º C to 77º C) [12]. This accelerated weathering test procedure has been performed on many different stone types, including granites, marbles, limestone, and sandstones. The procedure has shown that the strength loss for certain stone exposed to 12 to 16 cycles of accelerated weathering is approximately equal to one year of actual weathering for stone exposed to a temperate climate such as the Midwest United States.

Heating and cooling as well as freeze-thaw cycles are known to be a significant contributor to the deterioration of stone. The cyclic thermal expansion and contraction of stone minerals can also result in a breakdown of the stone’s structure over time. Moisture present in the stone which freezes, expands, will cause deterioration of the pore structure and/or bedding planes and result deterioration types described previously. Review of temperature data for freeze-thaw days and freezing periods recorded for a particular location provides a degree of understanding of the number of temperature cycles occurring. Obviously, for very warm environments the number of freezing periods will be minimal although temperature variations could be significantly high.
8. Conclusions

When considering these three stones or other local stones that have not been recently used in building construction, it is critical to understand the properties which make them unique. This understanding helps to prioritize repairs and determine the appropriateness of using the same material, if it is available, or using an alternate material without significantly compromising aesthetic and providing proven durability. Because stone is not a man-made product, its physical and aesthetic characteristics can vary significantly even within the same quarry, thus just because it appears to be the same material, does not mean it will behave as such.

Traditionally recognized stone properties include compressive, flexural, shear, and tensile strengths, density, abrasion resistance, coefficient of thermal expansion, and modulus of elasticity and rupture. In addition to these established properties, other properties that are frequently overlooked can contribute to premature failure of a stone cladding system. These properties include permanent volume change or hysteresis, freeze-thaw durability, chemical weathering, thermal weathering, effects of finish, orientation and permeability. Simply stated, these properties may reduce the strength and durability of the particular stone, which can lead to significant maintenance and repairs of the stone facades in the not-so-distant future.

References

[4] Chicago Tribune 1873, The Upper Peninsula; March 20, 1873, ProQuest Historical Newspapers.
CHARACTERIZATION OF MASONRY MATERIALS AND STRUCTURAL ANALYSIS OF THE ST MARY OF CARMEL CHURCH IN FAMAGUSTA

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Abstract

This paper presents experimental results for the characterization of the masonry materials of the 14th century St Mary of Carmel church in Famagusta, Cyprus. Stone specimens sampled from the church were subjected to laboratory tests to determine their apparent density, open porosity, modulus of elasticity, Poisson’s ratio and compressive strength. Furthermore, fractionation and XRD analysis of mortar samples was performed to investigate the mineralogical composition of the binder and aggregate fractions. Micro- and non-destructive in situ tests were also undertaken aiming to enrich the database of information regarding the properties of the masonry units. Experimental data were utilized for developing a finite element (FE) model that was subjected to non-linear time-history analysis. Useful conclusions regarding the seismic vulnerability of the monument under study are hence derived.

1. Introduction

The church of St Mary of Carmel is situated in the northwest corner of the medieval walled city of Famagusta. The structure was built in the 14th century. It is approximately 12 m high and consists of a single longitudinal nave that is 31.6 m long and 11.5 m wide (Figure 1). The nave is divided into four bays. At the east side a three-sided apse is formed. The roof was composed by ribbed vaults. Buttresses were constructed at the perimeter of the structure to provide support against lateral thrusts. The walls feature large openings which are formed by pointed arches. The average thickness of the masonry walls and buttresses is around 1 m. The main masonry material used in the construction of the building is a local calcarenite.
By the end of the 16th century the church had suffered a series of major earthquakes which took place in 1546, 1567, 1735 and 1741 [1]. These seismic actions probably led to its partial collapse and abandonment. Nowadays, the church is in a ruinous state. Only a small part of the original vaulted roof survives, covering the space above the apse at the east side (Figure 1d). The upper central part of the south façade is missing (Figure 1b), while the upper sections of the bell tower and of certain buttresses located at the south side have also collapsed. Inspections carried out over the last few years indicate that the masonry materials are in a rather poor state exhibiting signs of severe deterioration [2].

Currently, efforts are being made to assess the structural response of the monument and to determine appropriate methods for its conservation and long-term protection. Within this framework, the authors conducted a series of tests to characterize the masonry materials and numerically examined the dynamic behaviour of the structure.

2. Methodology followed for the characterization of masonry materials

The mechanical properties of the masonry materials were initially evaluated through non- and micro-destructive in situ tests on stone blocks (S2-9) at the interior and exterior of the structure. One stone block (S1) and two samples of jointing mortar (M1-2) were extracted
from the masonry walls of the church and were used in laboratory tests. The positions where stones and mortars were sampled from and/or subjected to in-situ tests are shown in Figure 2.

![Figure 2. Plan view of the St. Mary of Carmel church showing the positions where stones (S1-9) and mortars (M1-2) were sampled from and/or subjected to in-situ tests.](image)

### 2.1 In situ non- and micro-destructive testing of building stones

For the indirect evaluation of the stones’ compressive strength, rebound hammer tests [3] were undertaken on eight stone blocks (S2-9). An L/LR type concrete rebound hammer that generates an impact energy of 0.735 Nm was used for the tests. The hammer’s plunger was set perpendicular to the surface of the wall. The stone blocks examined were selected to be free from surface discontinuities (e.g. cracks, fissures, excessively eroded areas etc.). At each stone block, at least 10 readings were taken.

In addition to rebound hammer tests, micro-destructive drilling resistance measurements [4] were conducted using a cordless DRMS. A diamond drill bit with 0.5 mm diameter was attached to the test device in all measurements. The rotational speed was set at 600 rpm, while the penetration rate was set at 10 mm/min. The drilling depth was also set constant (1 cm). In order to obtain comparable results, drilling measurements were performed on the same stone blocks (S2-9) that had been subjected to rebound hammer tests.

### 2.2 Laboratory testing of building stones and jointing mortars

For the physico-mechanical characterization of the building stone, cylindrical cores with a nominal diameter of 55 mm were extracted from stone block S1. These were wet diamond sawn to form test units with aspect ratios of 1:1 and 1:2. The specimens obtained were oven-dried at 75 °C to constant mass before being subjected to standardized laboratory tests.

Apparent density and open porosity were measured through vacuum assisted water absorption and submerged weighting, following the methodology prescribed in EN 1936 [5]. Three test units with nominal dimensions diameter = height = 55 mm were examined.

For the determination of the material’s compressive strength, uniaxial loading tests based on EN 1926 [6] were undertaken on seven specimens with 1:1 aspect ratio. Elastic modulus and Poisson’s ratio were also assessed in accordance with EN 14580 [7]. Four specimens with approximate dimensions diameter = 55 mm and height = 110 mm were tested. Strain gauges
were attached on the specimens to monitor the axial and lateral deformations generated during compressive loading. Each specimen was subjected to three loading-unloading cycles up to a compressive stress of 0.8 MPa and was then loaded up to failure. The values of the elastic modulus and Poisson’s ratio were estimated from the stress-strain data measured during the third loading-unloading cycle. All load tests were conducted under deformation control at a constant loading rate of 0.2 mm/s.

The mineralogy of the rock material was examined through qualitative and semi-quantitative XRD analysis of a powder sample obtained from stone block S1. A locked-coupled continuous scan at 20 angles from 2° to 100° was performed.

In order to obtain information regarding the mix components of the masonry’s jointing mortar, fractionation of mortar sample M2 was performed. The sample was initially crushed to roughly segregate the aggregates from the binder. The processed material was then immersed in acetone. Repeated cycles of sonication and sieving through a 63 μm sieve were conducted to separate the binder and aggregate fractions. The dry weights of the fragments passing through (m_a) and retained on (m_b) the 63 μm sieve were measured. Based on the hypothesis that the material with particle size < 63 μm consists mostly of the binder, the binder:aggregate (b:a) ratio of the sample was computed as \( m_a : m_b \). Semi-quantitative XRD analyses were further conducted on the fractionated constituents of sample M2 and on powder originating from unsegregated sample M1. In all cases locked-coupled continuous scans at 20 angles from 2° to 70.064° were undertaken.

3. Experimental results and discussion

The experimental results are summarized in Table 1.

Table 1: Average experimental results obtained from laboratory tests on stone specimens cut from bulk sample S1 and from in situ tests conducted on stone blocks S2-9. The compressive strength reported was computed by applying the shape factors suggested in EN 772-1 [8] to the individual results obtained from test units with different dimensions.

<table>
<thead>
<tr>
<th>Property</th>
<th>Number of tests</th>
<th>Average value (± coefficient of variation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density (kg/m³)</td>
<td>3</td>
<td>1695 (± 1%)</td>
</tr>
<tr>
<td>Open porosity (%)</td>
<td>3</td>
<td>34.6 (± 2%)</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>7 (1:1 aspect ratio)</td>
<td>4.05 (± 22%)</td>
</tr>
<tr>
<td></td>
<td>4 (1:2 aspect ratio)</td>
<td></td>
</tr>
<tr>
<td>Elastic modulus (MPa)</td>
<td>4</td>
<td>9089 (± 25%)</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>4</td>
<td>0.220 (± 33%)</td>
</tr>
<tr>
<td>Rebound value</td>
<td>8</td>
<td>17.4 (± 19%)</td>
</tr>
<tr>
<td>Drilling resistance (N)</td>
<td>8</td>
<td>7.5 (± 66%)</td>
</tr>
</tbody>
</table>

The data obtained indicate that the stone has a rather low apparent density (1695 kg/m³) and a very high porosity (34.6%). The material also exhibits limited load-bearing capacity, since the average compressive strength recorded is ca. 4 MPa. The results of individual compression tests show noticeable deviations, varying from 3.2 to 5.5 MPa for specimens with 1:1 aspect
ratio and from 2.9 to 4.8 MPa for specimens with 1:2 aspect ratio. Elastic moduli computed from the stress-strain data recorded during the load testing of 4 specimens range from 6500 to 12500 MPa. The Poisson’s ratios evaluated from the same tests are between 0.14 and 0.29. Rebound hammer tests conducted on stone blocks S2-9 produced results within the range 10-21. The drilling resistances measured at the same positions are far more variable, ranging from 1.4 to 17 N. This was to some extent expected because the loosely bound grains of the tested stone can affect the testing procedure by introducing additional friction during the drilling process. To indirectly assess the load-bearing capacity of the stones, an exponential equation that correlates rebound value ($R_l$) with compressive strength ($f_b$) was adopted [9]:

$$f_b = \exp(1.332 + 0.053R_l)$$  \hspace{1cm} (1)

Moreover, a linear relation between the drilling resistance ($F_D$) and the compressive strength was developed using data reported in [10]:

$$f_b = 0.85F_D + 2.0$$  \hspace{1cm} (2)

Applying $R_l = 17.4$ to equation (1), results to a prediction of $f_b = 9.5$ MPa. For $F_D = 7.5$ N, equation (2) gives $f_b = 14.6$ MPa. This overestimation of the material’s compressive strength can be partly attributed to the natural randomness and inhomogeneity of the building stones and to material degradation encountered at different areas of the masonry.

Table 2: Mineralogical composition of building stone and jointing mortars.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Building stone (S1)</th>
<th>Unsegregated mortar (M1)</th>
<th>Fractionated mortar (M2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binder</td>
<td>Aggregates</td>
<td>Binder</td>
</tr>
<tr>
<td>Calcite</td>
<td>64%</td>
<td>77%</td>
<td>79%</td>
</tr>
<tr>
<td>Quartz</td>
<td>8%</td>
<td>9%</td>
<td>3%</td>
</tr>
<tr>
<td>Plagioclases</td>
<td>13%</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>Phyllosilicates</td>
<td>7%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aragonite</td>
<td>6%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gehlenite</td>
<td>-</td>
<td>1%</td>
<td>3%</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Halite</td>
<td>-</td>
<td>-</td>
<td>1%</td>
</tr>
</tbody>
</table>

The outcomes of the mineralogical analyses are presented in Table 2. Calcite is the most abundant crystalline phase in the stone material, while quartz, plagioclases, phyllosilicates and aragonite were also detected. This verifies that the stone is a bioclastic limestone (i.e. calcarenite). The high percentage content of calcite identified in both the unsegregated sample M1 and the binder fraction of sample M2 indicates that lime-based jointing mortars were used in the construction of the monument. Considering that calcite, quartz and phyllosilicates are the predominant minerals in the mortar aggregate fraction examined, it can be argued that local calcarenite sand was probably used in the mix design. The presence of gypsum in the mortar samples is presumably the result of secondary salt formation due to atmospheric pollution.

Fractionation of mortar sample M2 gave a b:a ratio of 1:1.5 ca. The assessed binder content is considered rather high and points towards a low strength mortar. It is worth noting that lime mortar mixtures with b:a ratios close to 1:3 were traditionally used in Cyprus.
4. Computational investigation of the building’s seismic response

4.1 FE modelling
In order to numerically examine the seismic behaviour of the structure, a FE model was developed in Abaqus/CAE (Figure 3); this was subjected to non-linear time-history analysis. The stone-mortar composite was treated as a homogenous continuum whose mechanical properties average the effects of the two interacting materials. The response of the masonry medium was simulated using a damage plasticity constitutive model [11].

Figure 3. FE model developed for the dynamic analysis of the St Mary of Carmel church.

The parameters required for the formulation of the constitutive law were mainly derived from experimental data (Table 1). The density and the Poisson’s ratio of the masonry were defined as $\rho_w = 1695 \text{ kg/m}^3$ and $\nu = 0.22$, based on the corresponding properties of the stone material. Based on [12], low-strength lime mortars have a compressive strength of $f_{m} = 1.40 \text{ MPa}$ and an elastic modulus of $E_m = 119 \text{ MPa}$. By applying the theory of homogenization of layered materials [13], the elastic modulus ($E_w$) of the masonry composite can be estimated as:

$$E_w = \frac{1+(h_w / h_u)}{1+(h_u E_u / h_w E_w)} E_u$$  \hspace{1cm} (3)

where $h_w$ is the thickness of the mortar joint (2 cm) and $h_u$ is the height of the masonry units (20 cm). The aforementioned geometric and mechanical characteristics give $E_w = 1157 \text{ MPa}$.

Response to compression was defined using a parabolic stress-strain relation [14]. The compressive strength ($f_w$) was estimated using the empirical equation [14]:

$$f_w = K f_b^{0.7} f_m^{0.3}$$  \hspace{1cm} (4)

For natural building stones, $K = 0.45$ [14]; this results to $f_w = 1.30 \text{ MPa}$. Non-linear response in compression was assumed to initiate at stresses exceeding 30% of $f_w$.

In tension, the medium’s response was considered to be elastic up to the maximum allowable stress. A linear loss of strength was assumed after cracking. The uniaxial tensile strength was set as $f_t = 10\% f_w = 0.13 \text{ MPa}$. The tensile fracture energy controlling the tension softening response of the masonry was defined as $G_t = 40 \text{ N/m}$ [15].
For the full definition of the yield surface, the following plasticity parameters were additionally specified: (a) dilation angle $\psi = 15^\circ$ [16], (b) eccentricity $e = 0.1$ [11], (c) ratio of the initial equibiaxial compressive yield stress to the initial uniaxial compressive yield stress $\sigma_{0b}/\sigma_{0c} = 1.16$ [11] and (d) parameter relating the second stress invariant on the tensile meridian to the equivalent invariant on the compressive meridian $K_c = 2/3$ [11].

Walls and buttresses were discretized into 3- and 4-noded shell elements with 6 degrees of freedom per node and 5 Gauss integration points through the thickness to account for out-of-plane bending. The two tower pillars at the west side were modelled using 2-noded linear beam elements attached to the cross-walls via common nodes. The approximate global size of the elements’ sides was set as 0.5 m. Pinned supports were defined along the walls’ base.

4.2 Dynamic analysis and numerical results

Dynamic analysis was completed in two successive numerical steps taking into account geometric non-linearity effects. Initially, the structure was analysed under dead loads using a general static solution procedure. Then, the seismic load was imposed adopting a dynamic implicit procedure with direct integration and a full Newton equation solver scheme. Upon the transition from the static to the dynamic step, the basal translational constraints along the $x$, $y$ and $z$ axes were replaced by ground accelerations acting in the same directions. The amplitudes of the seismic accelerations were defined in accordance with the accelerograms recorded in Limassol during the 1999 August 11th Earthquake (Figure 4). The duration of the selected seismic event is 30 s. The peak ground accelerations in the $x$, $y$ and $z$ directions are 0.149g, 0.167g and 0.090g, respectively.

Figure 4. Accelerograms of the $x$ (a), $y$ (b) and $z$ (c) components of the 1999 August 11th Limassol Earthquake.
The predicted damage distribution is shown in the contour diagrams of Figure 5, which present the maximum principal plastic strains computed at the elements’ integration points. Crack prediction lies on the hypothesis that the direction of the vector normal to the crack plane is parallel to the direction of the maximum principal plastic strains. Most major cracks form at 7.06 s, when the ground acceleration in the y direction attains its maximum value. Damage propagation from this point onwards is rapid due to the brittle nature of the masonry. The numerical model predicts that, in the event of the simulated earthquake, the structure will sustain significant damage. A major vertical crack is expected to develop at the south façade, at the point where the wall intersects with the tower pillar. In addition, vertical and diagonal cracks will occur above most arched openings due to stress concentration at these sections. Results also indicate that seismic action can cause extensive damage to the remaining part of the roof. Tensile cracking was recorded at the areas where the roof connects to the walls and at the ribs of the vaults. This raises concerns regarding the stability of the vaulted roof in case the building is struck by an earthquake with a magnitude greater than 0.15g.

Figure 5. Computed distribution of maximum principal plastic strains.

Figure 6 compares the variation of the relative out-of-plane displacement measured at the south and west walls’ central upper sections over time. Relative displacements were computed by subtracting the translation of the basal nodes along the x and y axes from the corresponding total lateral displacements of the two control nodal points at the top. The maximum relative displacement of the south wall is 16.5 mm in the x direction, while the maximum relative displacement of the west wall is 31.4 mm in the y direction. Considering that, for stone masonry walls, failure drift (i.e. loss of load-bearing capacity) can be in the order of 0.5%-3% [17], for the 12 m high walls hereby examined the limit out-of-plane displacement is in the order of 60-360 mm. Although the estimated relative displacements do not fall within the aforementioned limit range, the analysis shows that permanent deflections can develop at both the south and west walls. After 4.4 s, when the horizontal components of the ground acceleration reach approximately 0.025g, inelastic out-of-plane deformations are generated. Following the imposition of the peak ground acceleration, the two walls continue to oscillate around new equilibrium positions which are approximately 6.5 mm for the south wall and -25 mm for the west wall. The analysis predicts that residual inelastic out-of-plane

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deformations around 5.5 mm and -27 mm will develop at the upper sections of the south and west walls, respectively. Such permanent distortions would introduce eccentricities to the structure, increasing the probability of partial collapse in the event of a seismic aftershock.

![Figure 6](image_url)

> Figure 6. Time history of the relative displacement measured at the upper central sections of the south wall along the y direction (a) and of the west wall along the x direction (b).

### 5. Conclusions

This study presents the results of an experimental campaign that was undertaken in order to characterize the masonry materials of the St Mary of Carmel church in Famagusta, Cyprus. XRD analyses revealed that the structure’s walls were constructed of local calcarenite stone laid with the application of a rather weak lime-based mortar. The aforementioned stone has a highly porous structure (>30%) and a low compressive strength (ca. 4 MPa).

The experimental results were utilized for performing a non-linear time-history FE analysis of the building using real time accelerograms from Cyprus. Numerical results show that the absence of a stiff roof diaphragm precludes homogeneous structural response. As a result, walls tend to develop inelastic out-of-plane deformations. At the levels of seismic action examined, cracking damage was mainly concentrated at the surviving part of the vaulted roof and at sections adjacent to the openings. This indicates that appropriate interventions should be designed to avoid the formation of localized kinematic mechanisms.
Acknowledgments
The experimental work was partly funded by the United Nations Development Programme (UNDP), Partnership for the Future. The authors would like to acknowledge the support of P. Stylianou and his team. The Cyprus Geological Survey Department is also acknowledged for providing the accelerograms used in the dynamic simulation.

References
LIME BURNING TRADITION OF GOTLAND

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Abstract

As a part of the city wall in Visby fell down in 2012 a research project started to reconstruct the damaged parts. It was quite obvious that the rebuilding should be done with authentic local materials and traditional building techniques [1]. As we presented the research project we became aware that using local authentic lime mortar was easily done on Gotland but not elsewhere. Why? Well, the traditional lime production started in the 1100th century and never stopped. The knowledge about burning, slaking and storing lime in the Gotlandic way is known from olden days and was never lost or had to be fully reconstructed. This paper is about the lime burning tradition on Gotland and the tradition of making air lime as back in these days.

1. Introduction

The island of Gotland is situated in the Baltic Sea as part of Sweden. As Gotland had become Christian the knowledge of building stone churches and burning lime was adopted in 12th century. As most of Gotland is a lime stone rock from the Silurian age with stone suitable for burning, the transportation of lime stone never had to be far. Oven 100 churches where built between 11-14th century of lime mortar and the Hansa town Visby still show many 13th century trade houses and a medieval city wall of 3.4 km. Burning lime has been an activity well known on Gotland since those days, remains of small and large scale lime production can be found all over the island. What is unique for Gotland is that the lime production never stopped in our modern time. As the production ended for everyday use, it instantly started for restoration purposes [2].
2. Lime kilns on Gotland

Early remains of lime burning, show a tradition of small field kilns built up nearby the building site, see figure 1 [3].

Figure 1. Old drawing show a medieval field kiln found in the 19th century [3].

This type of field kiln has been in use until 1940’s by the peasants on Gotland and nowadays they are in use by our students.

Figure 2. Students have been building field kilns for lime burning each year on Gotland since 2000.
All around the Baltic Sea lime stone from Gotland was a common subject of trade during the Middle age, when unburned stone often was transported. In year 1622 the first preindustrial lime kiln where built followed by several more during the 17th century [3]. Shortly after Gotland again became a part of Sweden in year 1645 (after a Danish period between 1361-1645) the Swedish king set a tax fee on unburned lime stone leading to an up rise for lime burning industry. The industrialisation of lime production can be seen around the coast of Gotland nearby harbours and this is where lime for export was produced. For local use however the peasants were still allowed to burn lime in smaller kilns and field kilns.

![Image](image.jpg)

Figure 3. Three types of lime kilns can still be found in Barlåst on the upper east coast; from left to right we see a 17th century periodic lime kiln, a 18th century periodic lime kiln and a 19th century continuous lime kiln. The most reliable one was the 17th century kiln.

The type of lime burned for export was the most pure lime stone. It is a lime that is quite easy to burn; it can be burned in temperatures between 700-1200 °C without being dead-burned or over burned. It can be slaked in many different ways (wet, dry, earth slaked or as hot mix) and it can easily be transported as slaked lime in wooden barrels without losing in quality (to be compared to hydraulic lime from other regions [4]). Also analyses of mortars from Gotland show that is was the pure lime they used, known for its top quality also outside of Gotland [3,4].

The type of lime kiln for periodic use developed on Gotland (see figure 5b) during 17th century are still in use today [5,6] and also during 18, 19 and 20th century the old kilns were appreciated as they were very dependable giving a good quality lime. During 19th century the industrialisation led to continuous burning and lime kilns where built after bigger European models. Some of them where more successful than others and a few survived until the second world war with a lack of workers, fuel and building activity, put an end to local large scale lime industry. As the lime production of Gotland sunk it was invented and described in 1942 by Munthe [3], who found remains from 525 lime kilns from different time periods, see figure 4.
Figure 4. All known lime kilns of Gotland in year 1942, presented by Munthe [3].
Figure 5. a) The left figure show different ways of packing a periodic lime kiln on Gotland and b) the right figure is from 1805 when the Gotlandic type of lime kiln was described [3, 7].

Figure 6. Remains from different kinds of lime kiln; a) typical 17th century model, still in use 1964, b) large scale industry in use until 1946 and c) a continuous lime kiln for car coal in use in the 1860’s.
As the local masons of Gotland continued to prefer the traditional local lime putty above industrial lime powder the burning for local use in small scale continued anyway until 1964 nearby Visby [2]. In 1965 the production started in Hejnum as future demand from restoration architects and conservators all over Sweden required the white and fat lime putty that Gotland was famous for [8].

3. Lime slaking – local traditions

Knowledge from old times preserved a type of slaking technique called earth slaked lime [9,10,11]. It’s a slaking technique where the burned lime stone is placed unslaked in lime pits for many years. As the moisture from the ground slowly slakes the lime it gives lime putty with the best quality concerning workability, shrinking and flexibility [11]. The lime putty must be whipped before use in mortar and traditional lime whips are still in use for education. But also the knowledge and use of wet slaking and storing in lime pits as well as hot lime has been kept and developed until our days.

As the city wall of Visby was reconstructed it became clear that different slaking techniques can give mortars with very different properties [1]. When using the burned lime of Gotland masons prefer one slaking technique for bedding mortar (hot lime) another for render (earth slaked lime) and a third for lime wash (wet slaked lime). Old Swedish handbooks show that it
was known back in the days that lime from different regions should be burned, slaked and mixed in different ways according to their properties [12, 13]. Analysis show that fat air lime mortar was used both for bedding mortar, plaster, render and lime wash [1,9,14]. Many analyses of medieval mortars from Gotland in thin section shows lime with lumps that can be recognised as un-whipped particles from earth slaked lime [1,9, 11], see an example of mortar from Visby city wall in figure 8.

Figure 8. Thin section analysis of a 14th century bedding mortar of lime from Visby city wall, showing a typical un-whipped lime lump of air lime. In new produced mortars those lime lumps are found when using earth slaked lime. The width of the sample is equivalent to 4.5 mm.

What is unique on Gotland is that the local knowledge of lime production was never completely lost [2,3,4,5,7,8,15]. Today the traditional lime production take place in two different lime kilns of a type first constructed in 17th century and developed until 20th century [4,5,8]. Since year 2000 the students of our university have been burning lime in small filed kilns almost every year. The knowledge of field kiln lime burning has also been exported to other regions of Sweden from Gotland for development according to local conditions and traditions [16,17]. On Gotland we have spent the last two decades trying to reconstruct also the knowledge of the craftsmanship linked to the traditional lime and the lime rich fat mortars [1,9,10,14].

4. Conclusions

Together we must take a responsibility for preserving and developing this unique knowledge to future generations and to other regions that lost their knowledge. By using local lime in
restorations of the built heritage following the local tradition with high quality lime mortar we also contribute to sustainability.

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DEVELOPMENT OF MORTARS IN DENMARK FROM THE VIKING AGE UNTIL TODAY

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Abstract
Numerous chemical and structural analyses of mortars and renders of various ages at the Danish Technological Institute (DTI), Masonry Centre have revealed a very clear development of masonry and rendering mortars in Denmark through the last 1000 years. The history of Danish mortar and rendering begins in about year 1000 AD where the first masonry structures were prepared. For the first 900 years or so, strength development in mortars was based on carbonization of slaked lime alone. Until about year 1800 AD mortar was prepared by hot lime mortar technology; analyses show lime contents of 25-40 % (w/w). Around 1800 AD the hot lime mortar disappeared in Denmark and was replaced by a much weaker mortar consisting of a mix of sand and pre-slaked lime. For these mortars, the lime content was normally 7-14 % w/w.

The hot lime mortar had high compressive and adhesive strength and was the base of e.g. medieval structures in cathedrals and castles. The later mortars of lower lime content show weaker strength. This type of mortar is the normal in Denmark until the 1960s.

1. Introduction
Mortar in Denmark (DK) has a 1000-year long history, but in fact, the history takes its beginning 70 million years ago, in the geological Danian period, when limestone was formed. At that time, present Denmark was covered by a warm ocean. Millions of caccolites with calcium carbonate shells fell to the bottom and formed a deep formation of limestone. However, as the climate was warm and dry, nearly no material was washed out by rivers from the surrounding continents. Therefore, limestone formations had a very high content of CaCO₃. The contents of e.g. SiO₂, Al₂O₃ and Fe₂O₃ were very low (< 1 %) [1]. Thus, when this limestone is used for mortar, it have no hydraulic properties in practice.
These pure lime mortars harden by reaction with CO$_2$ from the air resulting in the formation of calcium carbonate. In contrast, hydraulic binders like cement and hydraulic lime, i.e. lime containing significant amounts of clay impurities rich in SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$, harden by reaction with water forming various water hydration products.

Over the years, DTI, Masonry Centre has performed chemical and structural analyses of a significant amount of mortars from historic Danish buildings. These have shed light upon the development of mortar in Denmark.

2. Mortars in Denmark

The history of Danish mortar begins in about year 1000 AD, where the first masonry structures were prepared. Chemical analyses show that from about year 1000 AD until the 18$^{th}$ century, masonry mortars with very high lime content (about 25-40 % w/w) were used. Mortars with such high lime content can only be made as a hot lime mortar, probably mixed in-situ by slaking the lime in the wet sand. The hot lime mortar technology produces mortars with high strength and flexibility, and normally very good adherence to bricks. These hot lime mortars have not only been used for bricklaying, but also for laying different kinds of natural stones. In Denmark, natural stones were mainly used in the early Middle Ages. These natural stones include granite, travertine, limestone, tuff, and sandstone.

The high content of lime results in high pH values of hot lime mortars. Combined with the increased temperature during lime slaking, the high pH can induce pozzolanic reactions of aggregates or even clay bricks by partly dissolution followed by precipitation of strength giving hydration products. These hydration products incorporates lime from the mortar and dissolved silicates or aluminosilicates from the aggregates or clay bricks. This will further increase the masonry strength [2].

The hot lime mortars with high lime content are primarily preserved in the ca.1750 medieval churches of Denmark (Fig. 1), and to a limited degree in abbeys, castles, and town houses.

Table 1 gives examples of chemical analyses of mortars from four different medieval churches in Denmark. Lime content of 24–42% w/w was found for the four mortars studied.

| Table 1: Lime and sand content in mortars from medieval churches in Denmark |
|-----------------------------|-------------------|-------------------|
| Period | Lime content (%) | Sand content (%) |
| Værløse church | 15$^{th}$ century | 24.4 | 75.6 |
| Farum church | 15$^{th}$ century | 35.0 | 65.0 |
| Åle church | Before 1536 | 37.0 | 63.0 |
| Rørvig church | 13$^{th}$ century | 41.6 | 58.4 |
Figure 1. Rørvig church. Behind the rendering mortar is the original masonry from the 13th century made of large medieval bricks and lime mortar with high lime content (see Table 1).

An extraordinary opportunity of sampling and further analysis became possible when Mårup church in Northern Jutland was to be restored due to the continuous erosion of the North Sea coast area. The church is built in the 13th century around year 1250.

The chemical composition is determined for 7 mortar samples extracted from the church. The mortars are primarily expected to originate from the construction in about year 1250 but also from renovations in about year 1500 and 1800. All 7 mortars are pure lime mortars with lime contents in the range of 28-43% w/w (49% for one sample). It is noticed that the mortar sample expected to originate from around year 1800 has a lime content of 30%.

Investigations in Maarup further included analysis of the mortar aggregate. In the laboratory, the aggregate was separated from the binder by heat treatment to 1000 °C, at which temperature the binder is decomposed. Separation of the aggregates allows determination of grain size distribution of the mortar sand by standard sieve analysis. The analyses from Maarup church showed typical, but very different grain size distribution in a mortar from about year 1200 and a mortar from about year 1500. In Figs. 2 and 4, the black lines indicate the current limits for standard mortar sand.

Figure 2. Grain graph, bricklaying-mortar, year 1200 (line mainly to the left).

Figure 3. Microscopy of bricklaying-mortar, year 1200. Image width is 2.5 mm.
Figure 4. Grain graph, bricklaying-mortar, year 1500 (the line that starts and stops in the middle).

Figure 5. Microscopy of bricklaying-mortar, year 1500. Image width is 2.5 mm.

The sieve analysis on the samples from the original, Roman masonry from approximately year 1200 shows a very steep grain size distribution where more or less all grains of sand are about 0.25-0.5 mm. As seen in Figure 3, the microscopy confirms that the aggregate in a mortar sample from year 1200 is very homogenous and even in size. The aggregate is mainly quartz, but in addition, there are also small amounts of feldspar and limestone.

In the mortar sample from 1500, the analysis shows that the aggregate has a so-called graded grain size distribution, which is typical for diluvial sand (Fig. 4). The finding is confirmed by the microscopy study that shows that the main part of the aggregate is quartz. But there are also amounts of feldspar, flint, rock fragments, and limestone (Fig. 5).

In agreement with the expectations of the given time of construction, the mortar from Maarup church is lime mortars with high lime content, most likely prepared by hot lime technology. Based on the analyses and the location of the church very close to the sea, the sand aggregate is expected to originate from sand dunes (Fig. 2). The steep particle size distribution falling outside the present limits of mortar sand (black lines in Figs. 2 and 4) have resulted in reduced mortar strength.

Analyses show that pure lime mortars with high content of lime were used throughout the Renaissance and until the 18th century. Towards the end of the 18th century, the lime content however decreased to about 15-20 % lime. Investigations of samples from Moesgaard Manor in Aarhus Denmark gives an example of this. Investigations of four mortars from the building dating 1779 reveals the use of pure lime mortars of lime contents 13-25%. The explanation for the decrease in lime content might be that the slaking and mixing processes were improved through the centuries. Hence, large unreactive lumps of lime were avoided and the required strength was obtained with lower content of lime.

At the end of the 18th century a new type of mortar developed. This mortar was a mix of sand and pre-slaked lime, i.e. Ca(OH)₂. The lime content of these mortars was about 7-8 %. This dramatic decrease in lime content was probably caused by a combination of increased demand for mortar and the fact that the country was very short of woods, and firewood, and it was
thus troublesome to establish the energy for burning of lime. These mortars were much weaker, regarding both compressive and tensile strength. This type of mortar was the most common in DK until the 1960s. The standards from 1945 demanded a lime content of at least 7.5% in masonry mortars and 9-13% w/w in rendering mortars.

In the early 19th century, Portland cement developed in England. Today Portland cement is the most commonly used active hydraulic binder, i.e. a binder that hardens upon reaction with water. The name Portland cement dates back to a patent by Joseph Aspdin in 1824. The name is said to have been chosen to call to mind Portland stone, a limestone quarried in the Isle of Portland in England having a high reputation as a building stone due to its quality and durability [3].

Soon after the development of Portland cement, it was imported to Denmark. This is witnessed by the investigation of two cement barrels salvaged from an English shipwreck dated 1857 near Esbjerg Denmark. Chemical analysis of the cement showed that its composition was similar to the composition of present rapid hardening CEM1. The cement was intended to be used for rendering of the local merchant’s house and pub in Ringkøbing, Denmark [4]. In 1911, E. Suenson describes in his Danish-language educational book on construction materials the use of Portland cement for masonry mortar [5]. In the textbook, Suenson refers to a cement composition containing ≈ 63% CaO and ≈ 22% SiO2. In addition, the textbook describes that for use as masonry mortar, the cement should be mixed with sand in the proportion 1:3 or 1:4 (cement:sand) according to volume. Depending on the type of sand, this corresponds roughly to about 1:4 (cement:sand) by weight corresponding to the present norm mortar C 100/4001. This is illustrated by the example below where a pure cement mortar of 24% cement among other types of mortars has been used as masonry mortar in a town house dating 1895.

At the same time, the so-called “bastard mortar” technology was developed. This combines cement mortar and weak lime mortar in a lime-cement mortar. The cement mortars described above contain about 20% cement (C 100/400) and are prepared dry. This mortar is very strong, but expensive and has poor plastic properties. On the contrary, the weak lime mortar prepared by mixing pre-slaked lime and sand is inexpensive and has good plastic properties. The two mortars are mixed in-situ in various proportions depending on the application. This results in a mortar of reasonable price, strength and plasticity. As the mortar is neither a cement mortar nor a lime mortar, it is referred to as “bastard mortar”.

Investigation of a Danish building from 1895 (Fig. 6) illustrates the use of the “bastard mortar” technology. The building is constructed using various clay brick materials and it is partly rendered and partly decorated. The composition of six mortars from this building were investigated by chemical analysis (Table 2).

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1 C indicates that the binder is cement and 100/400 indicates the weight relation between cement (100) and sand (400). In this notation, the binder content is always set to a total of 100.
Figure 6. Danish building from 1895.

Table 2: Chemical analysis of masonry and rendering mortars from a 1895-building. The CL formula gives the content of cement/lime/aggregate. For this notation, the sum of binder, i.e. cement and lime, is 100. The aggregate content is scaled according to this.

<table>
<thead>
<tr>
<th>Material type and description</th>
<th>Contents (% w/w)</th>
<th>CL-formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
<td>Lime</td>
</tr>
<tr>
<td>Sample 1 Masonry mortar</td>
<td>0,4</td>
<td>11,6</td>
</tr>
<tr>
<td>Sample 2 Rendering mortar</td>
<td>23,6</td>
<td>-1,5</td>
</tr>
<tr>
<td>Sample 3 Masonry mortar</td>
<td>1,9</td>
<td>12,5</td>
</tr>
<tr>
<td>Sample 4 Rendering mortar</td>
<td>5,0</td>
<td>12,8</td>
</tr>
<tr>
<td>Sample 5 Rendering mortar</td>
<td>7,6</td>
<td>12,3</td>
</tr>
<tr>
<td>Sample 6 Rendering mortar</td>
<td>2,2</td>
<td>34,0</td>
</tr>
</tbody>
</table>

The chemical analysis showed that sample 1 is a pure lime mortar with \( \approx 12\% \) lime, whereas sample 2 is a pure cement mortar with the approximate composition \( C \ 100/400 \). The cement content above 100\% illustrates the uncertainty associated with the chemical analysis and the assumptions regarding the chemical composition of the cement in use. Figure 7 illustrates the composition of the six mortars in a graph showing the sand content at the x-axis and cement content at the y-axis. The contents in relation to the CL-formula (Table 2) are used. For this notation, the sum of binder, i.e. lime and cement, is set to 100, and the content of aggregate is scaled to match this. Mortars obtained mixing the pure lime mortar (sample 1) and the pure cement mortar (sample 2) would result in mortars of compositions falling on the straight line between these two end points. From figure 7, it is seen that the composition of the mortars 3-6 are distributed around this straight line illustrated by the shaded area. These mortars are thus likely to have been obtained by in-situ mixing of the pure lime and cement mortars already.
present at the construction site. In general, the rendering mortars have a higher fraction of cement than the masonry mortars.

![Cement and sand content in “bastard mortars”](image1)

Figure 7. Cement and sand content in “bastard mortars”. The axis are scales according to the CL-formula notation.

Analysis and investigations done by DTI in connection with building examinations have shown that these “bastard mortars” have very good strength properties in relation to the cement content. In CL 50/50/700 mortars, the cement normally will provide at least 75 % of the strength. In “bastard mortars”, the strength effect of the cement is even higher.

### 2.1 Case study

The following case study provides results that clarify some of the tendencies in the development of mortars in Denmark. DTI has investigated a churchyard wall in Snejbjerg, Western Jutland, to determine mortar quality and characteristics to be able to recommend which mortars to use during the restoration of the wall. The wall is made of natural ashlar stone (Fig. 8). The age of the churchyard wall is unknown.

![Part of the churchyard wall in Snejbjerg](image2)

Figure 8. Part of the churchyard wall in Snejbjerg.
The examined area includes the southern part of the wall, and the examination was concentrated on a representative section of the wall. The dimensions of the wall are 120 cm high on the outside, 85 cm high on the inside, and 50 cm wide. The wall is covered on its top with in-situ cast segments of grey and extremely hard mortar, with about two meters between the joints. The mortar separates relatively easily from the wall underneath. Below the cast segments is a whitish mortar. This mortar has traces of broom strokes.

On the outside of the wall, there are 4-5 courses with fairly regular ashlars. It is obvious that the joints between the ashlars have been finished several times. The joints are mostly grey and strong, but a relatively pale mortar is estimated to be the original joint mortar. On both the south side and the north side of the wall, the assumed original mortar is pulled back from the front of the stones. On the contrary, the later repair mortars are rubbed all over the stone surfaces.

Inside the actual wall, there is a relatively weak masonry mortar. Mainly rough natural stones have been used on the inside (north side) of the churchyard wall and several different joint mortars are found here too.

The following samples were extracted:
1. The in-situ cast mortar covering the top of the wall.
2. Whitish mortar from underneath the cast mortar on top of the wall.
3. Mortar with humus or other organic content.
4. Strong joint mortar from the south side of the wall.
5. Masonry mortar from the south side of the wall.
6. Strong joint mortar from the north side of the wall.
7. Masonry mortar from the north side of the wall.
8. Assumed original joint mortar from the north side of the wall.

Samples 2-7 were analysed in a chemical laboratory to determine the moisture content and the composition of the mortars (results not shown). Studies done by DTI have shown that hygroscopic moisture in masonry materials corresponds to the content of soluble salts in wt%.

The mortar composition was determined for samples 1, 2, 7, and 8 by chemical analysis. The analysis determines the total content of lime, the content of unreacted lime, i.e. lime present as Ca(OH)$_2$, and SiO$_2$ soluble in 18.5% HCl at room temperature. The results of the analysis are shown in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unreacted lime, wt% Ca(OH)$_2$</th>
<th>Total lime content, wt% Ca(OH)$_2$</th>
<th>Soluble SiO$_2$, wt% SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1.37</td>
<td>12.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.86</td>
<td>9.38</td>
<td>3.21</td>
</tr>
<tr>
<td>Sample 7</td>
<td>0.22</td>
<td>8.36</td>
<td>0.13</td>
</tr>
<tr>
<td>Sample 8</td>
<td>0.64</td>
<td>12.6</td>
<td>3.28</td>
</tr>
</tbody>
</table>
The content of lime, soluble SiO₂ and the conditions mentioned below were used to calculate the mortar composition:

- Lime, cement, and sand were used.
- Cement contains 21.5 weight% soluble SiO₂ and 65.0 weight% CaO corresponding to a traditional Portland cement used in Denmark in the period from around the 1850s to about 1960.
- The sand does not contain lime grains.
- The part that is not cement contains 0.1 % soluble SiO₂.

From these conditions, the mortar composition was determined. The results are seen in Table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lime weight%</th>
<th>Cement weight%</th>
<th>Sand weight%</th>
<th>Mix proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.2</td>
<td>16.5</td>
<td>83.7</td>
<td>CL 101/-1/514</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
<td>15.1</td>
<td>88.2</td>
<td>CL 128/-28/748</td>
</tr>
<tr>
<td>7</td>
<td>8.5</td>
<td>0.1</td>
<td>91.4</td>
<td>CL 1/99/1061</td>
</tr>
<tr>
<td>8</td>
<td>-0.1</td>
<td>15.4</td>
<td>84.7</td>
<td>C 100/552</td>
</tr>
</tbody>
</table>

* The mix proportion states the relative content of lime(L)/cement(C)/sand. The content of lime and cement sums up to 100.

From the results in Table 4, we can see that:

- The original bricklaying mortar (sample 7) is a pure lime mortar
- The mortar underneath the cast mortar covering the wall (sample 2) and the original joint mortar (sample 8) can be regarded as the same kind of mortar, i.e. a strong cement mortar
- The calculation showing a negative lime content can be caused by a pozzolan reaction between non-hardened lime and aggregates
- The in-situ cast segments covering the wall are made from pure cement mortar

Based on the material analysis we estimate that the wall is built towards the end of the 19th century. The mortars are characteristic for this period:

- Pure 8.5 % lime mortar for the construction. The lime mortar is used between natural stones with no or only little water absorption.
- The segments covering the wall are cast with a pure cement mortar
- The layer underneath the cover and the original joint mortar are both strong cement mortars. The mortars are quite pale and might have had a small lime content, and in that case they must have been made as “bastard mortar”, i.e. a mix of pure lime mortar and pure cement mortar.

The calculations of hygroscopic moisture show high salt contents in the strong cement mortars. The explanation might be that the area around the church is a former village. Studies
made by DTI, Masonry Centre, show that in places like these the solution of salt in the ground can be very high. Normally, calcium nitrate is found, caused by human and animal activity through maybe 1000 years [2]. Numerous mortar studies done by DTI have also shown that moisture, and thereby salts, concentrate in cement mortars rather than in lime mortars. In this case, we see that the content of hygroscopic moisture is lower in the construction mortars (which are lime mortars) than in the strong cement mortars. High salt content can induce degradation of masonry materials. Especially the original joint mortar seems to have been exposed to salt weathering.

3. Conclusion and discussion

A picture emerges of a mortar history where mortars with high binding material content were predominant through the Middle Ages and until the 18th century. The mortars with high binding material content were mainly pure lime mortars, however with the use of different kinds of sand and water content. You are not in doubt when you face and touch a hot lime mortar. The whiteness due to the high lime content, the strength, and the structure is unmistakable. Despite the prevalence of this type of lime mortar in Denmark, the hot lime mortar technology is rarely used in connection with restoration works on buildings from the relevant period, e.g. manors, fortresses, castles, churches, and town houses.

Until cement was introduced in the 1850s, Danish mortars based on pure lime without any hydraulic properties, were predominant. After the introduction of cement in Denmark in the middle of the 19th century, it was used right away in mortars: initially for rendering and joints, later on as part of the masonry mortars. The development of the “bastard mortar” technology made use of the strength of the cement mortar and the plasticity of the lime mortar at the same time. The mortars used in Denmark today have in fact the same mix proportions as the earlier “bastard mortars”, but as the latter had both high plasticity and strength properties at the same time, the mortars of today do not seem to be as appropriate. This regards both wet mortars (lime mortars with cement added at the building site) and dry mortars (premixed CL-mortars with water added at the building site). So the mortars that were used in Denmark earlier with great success are not used anymore. Slaking and mixing technology prevail the exact mixing proportions.

References
SALT CRYSTALLIZATION LABORATORY TEST WITH A COMPLEX BRINE

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It is well known that in buildings and monuments salts are one of the most important weathering factors. When analysing weathering products present in monuments a mixture of several different salts are always found. The most common salts are chlorides, sulphates and nitrates of sodium, calcium, potassium, magnesium, etc. Several authors tested complex brine crystallization processes under different environmental conditions or performed crystallization tests on laboratory stone samples using also a mixture of salts. In both cases they found that the results are different from those obtained with single salt compositions (see review in [1]).

We realised non-standard salt crystallization ageing tests using single salt solutions (NaCl, Na₂SO₄) at 6% wt and a mixture of them at 12% wt (6% NaCl and 6% Na₂SO₄). These one week cycles consisted of an immersion phase, followed by a two days drying, and four spraying/drying one day cycles. Drying temperature was 50°C. The salt crystallization test has been modified to simulate more realistic and less aggressive conditions. 7 Cycles have been done. Samples have been weighted after every wetting and drying period and have been photographed after every drying period.

As salt weathering can be also a consequence of crystallization/deliquescence cycles, after the crystallization cycles, samples have been subjected to 14 relative humidity cycles at 50°C, one week at low RH (5%) and one week at high RH (90%). Once again the behaviour of samples containing several salts is different from that of samples containing one unique salt.

In order to investigate the effect of stone microstructure on weathering process three different building limestones, with quite a similar mineralogical composition but with quite different pore systems, have been used. The selected stones are Lutetian, Caen and Vernon stones. A description of these stones can be found in [1].

ECOS RUNSALT model has been used to model the salt volume evolution as a function of environmental conditions during experiments. The main conclusions are:

- Complex salt brines produce less damage than single salt solutions.
- Caen limestone is the most affected by salt weathering which can be explained by the smallest size of its pores.
- Changes in relative humidity can be as dangerous as crystallization cycles by salt supply.
- Salt volume variations cannot explain the damage induced in samples by salts.

References

WEATHERING, MASONRY AND MODERN MOVEMENT

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This paper investigates the relations between Modern Movement’s masonry buildings and the idea of patina and authenticity. There is a schism between Modern Movement’s idea and practice and the idea and practice of patina. Modern Movement’s rejection of history and ornament was also often a rejection of building details, which were carefully constructed to delay and control the ageing processes of a building. The term weathering describes both the patina and deterioration of a building, but also the building details, which delay the deterioration and controls the patina process over time. The term weathering is investigated by architects David Leatherbarrow and Mohsen Mustafavi in the book On Weathering: The Life of Buildings in Time (1993) and the geographical specificity of a building is central.

The invention and use of reinforced concrete became iconic for Modern Movement’s international style and a mean for early Modern Movement’s architect’s desire to free them self from historical ornaments and style. It provided architects with the white paper needed to start over with a tabula rasa. Following, architects incorporated Modern Movement’s ideas into a regional – geographical and cultural – context. Brickwork was used to root the ideas of Modern Movement in Danish building culture and it seems possible also as a mean to construct buildings better fitted to Danish weather conditions etc.

The adaption of Modern Movement in Danish building culture and the execution of Modern Movement’s buildings in masonry raises a number of dilemmas regarding conservation: The weathering – the patina and the traces of time – is considered important when working with historical buildings and is connected with the idea of authenticity and age value. One may argue that in the case of Modern Movement’s architecture, it is the building as a monument and a set of ideas that is worth preserving rather than the physical building materials. Yet, when it comes to Modern Movement’s masonry, there’s a schism between the well tested, long lasting and solid material routed in a regional building culture and the Modern Movement’s ideas.

This paper is interested in the relations between Modern Movement’s ideas on buildings in time and the ability of weathering of Modern Movement’s masonry buildings in Denmark. In his project drawings, Danish classicistic architects C.F. Hansen demonstrates intentions of weathering when prescribing the patina in the façade drawings. Is there a similar coherency between Modern Movement’s architect’s project drawings and writings on a building from before it was raised and the building is it stands today regarding weathering? As an example, project drawings and writings on selected works from the Modern Movement by Danish architect Kaj Gottlob is studied and discussed in relation to the building as it stands today.
INTERIOR INSULATION RETROFIT OF A BRICK WALL USING VACUUM INSULATION PANELS: RE-CREATION OF CULTURAL HISTORICAL VALUES IN BUILDINGS FROM BEFORE 1945

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Extended Abstract

The Swedish housing stock is once again in focus for national energy savings, as it was after the oil crises in the 1970s. The need for renovation is equally urgent in older stocks of housing, also in those that already have been renovated but are in need of further interventions. The first part of this project concerns inventorying of building components in buildings from before 1945 in need of a second major renovation. The focus of the inventorying is energy performance, moisture resistance, long-term durability and thermal comfort. The results from the inventories will be used to investigate alternative and improved solutions for re-renovation to recreate e.g. architectural details and cultural historical values. The possible thickness of the insulation layer is limited by the existing construction. Vacuum insulation panels (VIPs) require less thickness than conventional insulation materials to reach the same thermal resistance [1]. Therefore, it could be more appropriate to use VIPs than conventional insulation materials when retrofitting the building envelope of listed buildings. In a previous study [2, 3], a brick wall with wooden beams was insulated on the interior with vacuum insulation panels (VIPs) in a laboratory. It was shown that adding interior VIPs can reduce the energy use substantially in brick buildings. Adding interior insulation decreases the temperature during the cold season, which results in higher relative humidity. In the wooden beams, the moisture content increased more in the end of the beam than close to the interior surface of the brick. There was no significant difference between the RH in the wooden beam ends in the case with and without VIPs.

References


CONSOLIDATING EFFECTS OF NANO-LIME PRODUCTS ON POROUS LIME RENDERS AND LIMESTONE

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Abstract
In many sectors of the industry it is currently possible to observe a growing interest in the development and application of nanotechnologies and nanomaterials. The latter have been applied, among others, also in the field of conservation of architectural heritage. One example of this application is the consolidating treatment of disintegrated lime mortars and limestone with nanoparticles of calcium hydroxide dispersed in alcohol.

The study presented in this article was focused on the consolidating effects of CaLoSiL E (nanoparticles dispersed in ethanol) and CaLoSiL IP (in isopropyl alcohol) applied on lime based substrates, namely porous lime mortars and porous limestone. As nanolime particles in the consolidating product CaLoSiL have a size with diameter in range 50-200 nm, the degraded building material to be treated should ideally contain much larger pores or cracks to absorb the liquid consolidant effectively into its pores structure. For the experiment presented here, porous Maastricht stone with pores size 48 μm and weak lime mortars with significant part of pores with a diameter 10-100 μm were used. Besides the mechanical properties of the treated specimens of mortar and stone (compressive and flexural strength), the influence on porosity and the colour of building materials was also monitored. The consolidation treatment with nanolime was carried out by slowly impregnating the surface of mortar or stone specimens with liquid consolidant up to full infiltration, by means of a syringe. The amount of the product applied was observed and subsequent treatment cycles with the same product were carried out a few days later, on fully dried material. Various concentrations of nanolime in the products were tested (15 - 50 g/l).

All tested nano-lime products penetrated well into all mortar and stone samples. The greatest strengthening effect was observed for the poorest mortar (1:9), which showed eight times higher compressive strength after 10 applications of nanolime. The measured flexural strength was three times higher than the initial one after 10 treatments and the water accessible porosity slightly dropped, from 32% to 28.8%. It was concluded that 5-7 repeated treatments of CaLoSiL E 25 can be recommended for the consolidation of very weak lime mortar with bad cohesion and 3-5 treatments for the consolidation of mortar with better cohesion. In the case of the Maastricht stone, 2 repeated treatments with CaLoSiL E 25 performed the best. It should be noticed that high concentrated product (50g/l) and higher amount of applied nanolime led to a change of surface colour to whitish tones, which may be considered in some cases unacceptable.

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Historical Masonry

Edited by
Inge Rörig-Dalgaard, Ioannis Ioannou

RILEM Proceedings PRO 110

This volume contains the proceedings of the MSSCE 2016 conference segment on Historical Masonry. This conference segment is one of the many events within the wider area of Civil Engineering taking place in the framework of RILEM Week 2016 and MSSCE 2016. The idea behind its organization was to revitalize interest in Historical Masonry within the RILEM community.

The present conference segment deals with theory, modelling and results from experimental investigations within the wider field of Historical Masonry. The topics covered include masonry materials (characterization and reproduction), measurement techniques, mechanisms of masonry decay and methods of assessing and protecting masonry. Papers featuring in the proceedings present state-of-the-art knowledge that extends to some interesting case studies, which both practitioners and people working in the academia should find appealing. All contributions have been peer-reviewed.

The event “Materials, Systems and Structures in Civil Engineering MSSCE 2016” is scientifically sponsored by RILEM. The event is hosted by the Department of Civil Engineering at the Technical University of Denmark and is financially sponsored by a number of independent foundations and organizations. The conference segment on Historical Masonry, in particular, is sponsored by Director Ib Henriksens Foundation and the Danish Lime & Brickworks association.

Working together to create a platform for collaboration on Historical Masonry has been a joy! We hope that you will find the proceedings interesting and worth reading. May this conference segment be the starting point for increased activity within RILEM in the field of Historical Masonry!