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JACOPO BONETTO, SIMONE DILARIA,
CATERINA PREVIATO

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Fabric of a binder- rich lime mortar with pores after plant fibres and silica-rich binder-related inclusions.

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Keynotes

MARIE D. JACKSON
University of Utah, Salt Lake City, Utah, USA

Reactive aggregates in the mortars of ancient Roman concretes: Clues to chemical and mechanical resilience

Abstract
Recent investigations into reactive aggregates in Roman mortars provide new insights into how these materials influence the extraordinary chemical and mechanical resilience of concrete in ancient architectural and marine structures. Reaction of aggregates (and cementitious components) with interstitial fluids leads to in situ production of diverse structurally disordered, poorly crystalline, and crystalline silicate binding phases, which reinforce cohesion long after pozzolanic consumption of portlandite is complete. Documentation of transport of pumiceous tephra, pulvis puteolanus, through the Mediterranean region further emphasizes builders' comprehension of the importance of these reaction processes to the longevity of diverse concrete structures. An arc-shaped bending test that intersperses periods of recovery between load cycles introduces a more relevant description of long-term material viability than initial strength for Roman analog mortars. The integrated results of these investigations provide a fresh context for studies of fracture morphologies and repair, recycled aggregates and, potentially, a circular economy in Roman construction.

Bio
Marie Jackson is a research professor in the Department of Geology and Geophysics at University of Utah, USA. Her collaborative investigations in archaeological science, materials science and pyroclastic volcanism describe cementitious processes in ancient Roman architectural and marine concretes and young basalt at Surtsey volcano, Iceland. She applies Roman methods of concrete production to environmentally-friendly, glass-based analog concretes and implements an innovative arc-fracture test that measures ductility, fracture toughness and repair. She hopes to introduce ancient Roman principles of concrete longevity and resilience to the production of modern concrete composites.

CARLOS RODRIGUEZ-NAVARRO
University of Granada, Granada, Spain

Learning from the past to build the future: Ancient lime-based mortars inspire new formulations for built heritage conservation and sustainable construction

Abstract
Aerial and hydraulic lime binders have been used by many ancient civilizations since the Early Neolithic. They were, however, phased out after the invention of Portland cement. Yet, cement's incompatibility with ancient masonry has resulted in the revival of lime as a compatible (and more sustainable) binder for built heritage conservation and modern construction. Still, lime shows some shortcomings, such as slow setting and carbonation hardening, and lower strength as compared with cement, limiting its current applications. There is, however, evidence regarding the outstanding strength, durability and resilience of lime-based mortars and plaster present in structures built by ancient civilizations. Here we present detailed studies of lime-based mortars and plasters present in such ancient structures which unveil the secrets of ancient masons, paving the way for the design, via reverse engineering, of novel paleo-inspired lime-based mortars and plasters with improved properties and performance. It is shown that paleo-inspiration combined with reverse engineering approaches can result in the development of novel functional, compatible, durable, and sustainable lime-based binders for a better future built environment.

Bio
Carlos Rodriguez-Navarro is full professor at the Department of Mineralogy and Petrology, University of Granada, Spain. Previously, he was a research fellow at the Getty Conservation Institute, Los Angeles, U.S.A. (1995-1999). His research focuses on mineral formation, and weathering and conservation of cultural heritage, with a focus on lime-based binders. He has published over 100 papers on salt damage, nanoscale processes during chemical weathering, bacterial mineralization, functional and biomimetic lime mortars and plasters, and mineral carbon capture and sequestration. He is a fellow of the Mineralogical Society of Spain, Editor-in-Chief of the European Journal of Mineralogy, and Associate Editor of several international peer-reviewed journals. He holds BS and PhD in Earth Sciences and a MS in Conservation Science from the University of Granada.

IOANNA PAPAYIANNI
Aristotle University of Thessaloniki, Thessaloniki, Greece

Why use Lime-based Mortars for repairing monumental structures?

Abstract
Lime-based Mortars (L-b-M) were used in construction from antiquity up to the domination of cement in 20th century. After failures observed in repaired monumental masonry structures with cement-based mortars, the use of them has been reconsidered. In the last 30 years, L-b-M have prevailed in restoration works to ensure the compatibility of interventions.
The easy availability of the L-b-M constituents, the simplicity in mixing them, the increase of their strength with time and the ability of L-b-M to incorporate additives or/and admixtures for improving their performance, are some of the basics that make their use in repair works realistic and effective up to nowadays. Microstructure of L-b-M and related properties such as porosity, microcracking, stress-strain behavior, dimensional stability and long-term performance, are presented comparatively to cement-based mortars. Significant advances in certifying the quality of L-b-M and their application have been made. There are limits in using L-b-M, but extending their use to meet increased durability requirements is possible in modern times.

Bio
Ioanna Papayianni is Emeritus Professor at the Aristotle University of Thessaloniki, Greece, specializing in building materials and historic preservation. With degrees in Chemistry and Civil Engineering, she holds a PhD in Civil Engineering. Her research focuses on sustainable interventions in historic structures, concrete durability, and the use of pozzolanic materials. She has led numerous national and European research projects and supervised 17 PhD theses. A key figure in scientific associations and committees such as RILEM and IALA, she has organized several international conferences and seminars. She has authored over 200 publications and contributed significantly to the field of construction materials and conservation.

GILBERTO ARTIOLI
University of Padova, Padova, Italy

Ancient binders: their role and history

Abstract
Literature on ancient binders systematically focuses on the chemical/mineralogical properties of the material, often disregarding the structural or architectural mode of use. Here, we critically examine the occurrence and use of ancient binders in architecture, since they encompass a variable range of technological, social, and anthropological significance. The apparent discontinuity of the technological development of binders in antiquity will also be discussed, together with the archaeological evidence in different geographical contexts.

Bio
Gilberto Artioli is a professor of mineralogy, crystallography and materials science at the University of Padova. He received a Laurea Degree from the University of Modena and a PhD from the University of Chicago. His interests focus on mineralogy, crystallography and materials science. His scientific expertise encompasses the use of combined techniques, including those based at large scale facilities, for the investigation of complex materials, including natural and industrial materials.

Topic 1

Characterization of historic mortars and masonry structures. Sampling and test methods

DOMENICO MIRIELLO

AI-Driven Acceleration of Archaeometric Analysis in Ancient Mortars: Efficient Data Interpretation from Image Analysis

Until recently, code was written by computer programmers proficient in the languages in which the programs were to be written. On November 30, 2022, OpenAI made its first public release of ChatGPT based on GPT-3.5, a neural network developed and specifically trained on large language models by OpenAI. Since then, the development of AI has accelerated significantly. With the advent of subsequent models of ChatGPT, especially GPT 4.0, the model is not only supposed to answer higher-order thinking kinds of questions but also will read and interpret in a meaningful manner files in all types of format that are drag-and-dropped directly into the chat. With the arrival of ChatGPT 4.0, this has opened opportunities for researchers not typically familiar with programming languages to new areas-for instance, Chemistry, Biology, Geology, Archaeology, and archaeometry-thus enabling them to produce their own solutions by effectively leveraging ChatGPT in generating computer code.

The implementation of ChaGpt greatly increased the development of competing artificial intelligence models (Bahriniet al. 2023), which in a very short time led to the development of "Mistral AI" (Hou and Lian 2024) and "DeepSeek" (Marcer et al. 2025).

Using the iterative approach proposed by Miriello and De Luca (under review in "Archaeometry"), some specific tools was created in python code through the combined use of several large language model's Artificial intelligence tools, such as "ChatGPT", "Mistral AI" and "DeepSeek".

The tools presented in this work try to improve and simplify some image analysis processes, such as the study of mortar aggregate (especially thresholding techniques), routine petrographic analysis of the samples and data interpretations.

A selection of case studies on ancient mortars with different types of aggregate (pozzolan-based, carbonate-based, cocciopesto and siclico-clastic based) will be presented. The tools developed improve aggregate segmentation processes, compared with traditional tresholding methods, allowing to segment even problematic minerals and rock fragments. Such tools, in addition to improving segmentation processes, allow for rapid quantitative processing related to the aggregate, such as the grain size distribution (e.g. cumulative frequency curve) and numerous descriptive statistical parameters.

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ANTHONY J. BARAGONA, MIRKO HECKERT-SCHULERI, STEFAN ENGHARDT, JOHANNES WEBER

Applied multi-energy CT for the analysis of Roman wall painting plaster fragments

1. Introduction

1.1. Background and Scientific Techniques

A plurality of plastering methods for wall paintings can be seen at the frontiers of the Roman Empire. These likely represent adaptation of local artisanal techniques to traditions originating in the Mediterranean basin. It is additionally apparent that differing plastering methods were used based on the function of the room, for example that a room highly visible to visitors would not only exhibit paintings of the highest quality, but these paintings would be on a plaster support and preparation layers of the highest quality as well[1a-d]. This observation is important when analyzing wall painting plaster from the former provinces of Noricum and Germania Inferior (today's Austria and Germany) as most of the material available for study is found in a fragmented state, and thus the original context of the wall paintings and much of what they depicted is lost.

While presenting a puzzle for archaeologists, conservators and restorers, the fragments do provide the opportunity for highly detailed, non-destructive, archaeometric study by X-ray computed tomography, which is not generally possible with in situ or large ex loco wall panting panels. This study presents the use of a still under-development method of multi-energy computed tomography (MECT) that produces images images with enhanced contrast, enabling a clear distinction between binder and aggregates, thus allowing a researcher to obtain archaeometric data that can be used to understand building traditions from several Roman provincial archaeological sites. The possibilities for what can be learned from beneath the painted surface in mortar fragments that have lost most of their context can be demonstrated by this non-destructive, minimally invasive (the fragment must be placed in the CT device) method[2-3]. An example of the type of imagery produced is shown in Figure 1 that follows.

1.2 Results/ Summary

From high-resolution ME-CT scans, a wide range of archaeometric data were produced through digital image analysis[4]. The type of data produced are briefly summarized in Table 1 below, which compares classical petrographic methods, i.e., microscopy and SEM-EDX of thin sections, with ME-CT. A quick glance at the table shows that the obtained results from this type on non-destructive, minimally invasive technique shows great promise; the authors intend to continue to both refine their techniques, as well as continue to use them for the analysis of historical building materials. This presentation illustrates the archaeometric potential of this technique; the technique itself is the subject of a separate presentation by Mirko Heckert-Schuleri.

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1 See for example: a) Santner (ed. 2007), b) Laken et al. 2018, c) Riedl 2007, d) Tober 2014.
2 Heckert et al. 2020.
3 Heckert-Schuleri et al. 2025 (under review).
4 The authors are in the process of assessing the applicability of machine-learning techniques to automate this process.

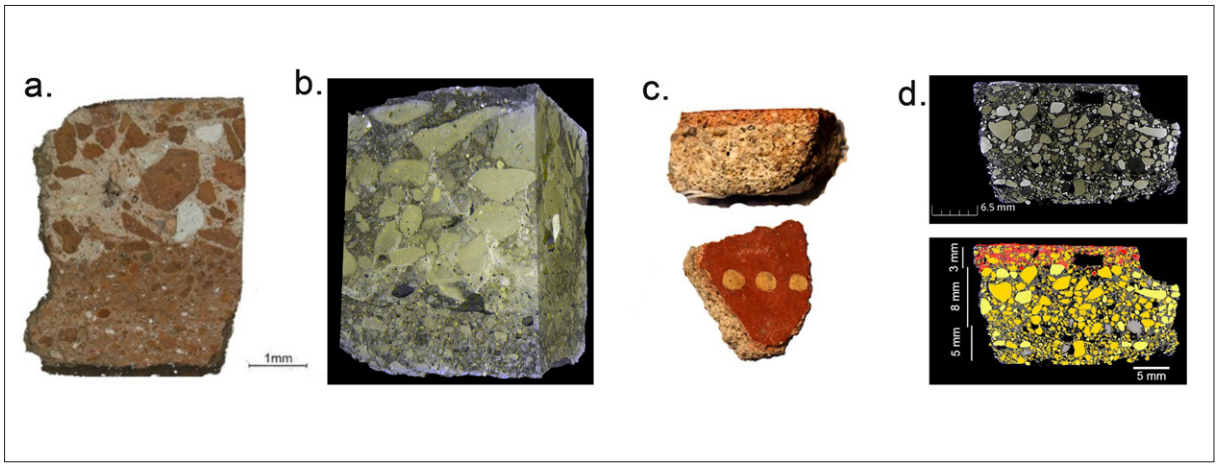

Figure 1. Two examples of Roman mortar analyzed by MECT. a., b.: a multi-layered, painted, cocciopesto mortar from Xanten and a 3D CT model of the same; c., d.: a wall painting fragment from Iuvavum, a MECT-generated virtual section, and a pseudo-colored image of the same

Archaeometric Desideratum	Thin section OM and SEM	ME-CT(non-destructive)
Plaster Layering/ Stratigraphy	+	+/-
(macro) porosity	+	+
Binder-to-Aggregate Ratio	+	++
Aggregate Granulometry	+/-	*TDB*
Aggregate Identification	++	*TDB*

Table 1. Efficacy of Image Analysis of MECT scans as compared to thin section microscopy ++ - excellent result, + good or comparable result, +/- mixed results, requires interpretation, TBD = Still a work in progress with this method.

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Mortar characterization with Multi-Energy CT – B:A ratio and granulometry without invasive sampling?

1. Introduction

Multi-Energy Computed Tomography (ME-CT) yields pseudocolour volumetric images of the inner structure of mortar samples. This enables the non-invasive determination of quantitative mortar parameters. This work presents an approach to determine B:A ratio and granulometry from ME-CT data. It will be mostly focussed on artificial samples prepared to compare this method to acid digestion and sieve analysis, a standard method for mortar analysis. Anthony Baragona will focus on the petrographic potential of ME-CT illustrated by the application of this technique to ancient mortars in another presentation at this conference.

2. Multi-Energy CT

X-ray Computed Tomography (CT) is a widely used tool to non-destructively gain information about the inner structure of object. Unfortunately, it often yields only a very low contrast between lime or cementitious binders and quartz grains, rendering it practically useless for the study of the vast majority of mortar samples. An exception is the determination of (macro) porosity of mortars[1].

ME-CT can enhance the contrast between different materials. It allows for the computation of 3D representations of the effective atom number (Z) and the density (ρ) inside the sample as well as the generation of pseudocolour images of virtual cross sections (Figure 1). The presented method was developed by the authors and is currently being refined with the focus on the characterisation of historic mortars[2]. It can be performed at standard cone beam CTs with our open-source evaluation software[3].

For mortar analysis, the pseudocolour ME-CT results show a clear contrast between quartz and binder, due to the different ρ and Z of these materials. Even the contrast between calcite and lime-binder is often acceptable. The CT measurement can be performed on fragments of various size, as long as they fit into the device. As the scan resolution is related to the size of the investigated volume, it's beneficial for large fragments to investigate only an exposed corner of the sample.

3. Determination of quantitative mortar parameters

In order to evaluate the mortar analysis with ME-CT, several mortar samples have been produced with lime as binder and fluvial sand and/or crushed marble as aggregate. Some samples have been produced with sieved aggregates to remove grains smaller than 0.2 mm.

3.1 B:A ratio

With the relatively good contrast between binder and aggregate in ME-CT it's possible to automatically determine the type of each voxel in a region of interest with digital image analysis. This can be done

1 Brunello et al. 2021.
2 Heckert-Schuleri et al. 2024.
3 Heckert, Enghardt, Bauch 2020.

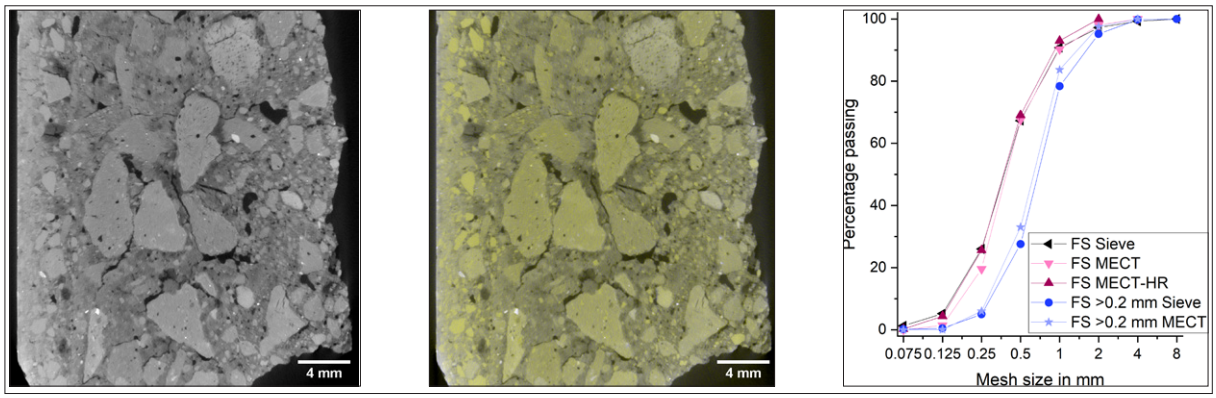

Figure 1. Stratigraphic slices of a roman mortar sample from Colonia Ulpia Traiana, left: conventional CT, middle: ME-CT. Several mortar layers are visible, the left layer has a high binder density and mostly quartz as aggregates, best visible in the ME-CT image. The middle layer contains crushed bricks. Right: Granulometry chart for 2 samples made from fluvial sand (FS), measured with ME-CT and acid digestion and sieve analysis. One sample was prepared without grains smaller than 0.2 mm. HR stands for a scan with high resolution (14 µm), the voxel size of the other measurements was 21 µm. We thank Dr. Elisabeth Krieger and Dr. Bernd Liesen from Archäologischer Park Xanten for access to the fragment.

with simple thresholding, more sophisticated methods like a random forest classifier implemented in the software Ilastik[4], or a neural network. The data categories are in this case: background, pores, binder and aggregates. Summing up the voxels in each class yields the B:A ratio as well as the (macro) porosity. These 3D results are comparable to the 2D ones from PLM images. To compare this numbers with results of acid digestion one needs to know the density of aggregates and binder. For lime binder the density might encompass values from 1 g/cm³ for newly prepared samples to almost the density of calcite (2.6 g/cm³) in historic samples. This is due to the micro-porosity that's invisible in CT. Still, the CT-data can be used to determine the density of the binder, if standards are available.

3.2 Granulometry

To calculate granulometry charts from ME-CT data, one first needs to be able to see all grains in the ME-CT image, so fine grains need a high resolution. Then, the image must be classified again as described above. To label the individual grains a watershed segmentation can be performed on the voxels classified as aggregates. This yields the 3D-data of the shape of all aggregates in the region of interest, say a cube with edges in the cm range. This is a great source of information to study historical building methods. However, it's not trivial to calculate a granulometry chart comparable to sieve analysis from this data. It's part of our ongoing research and various approaches will be presented. Currently the favoured approach is to approximate the aggregates as ellipsoids. Then the lengths of the axis of the ellipsoids can be compared to the mesh size of the sieves. For the granulometry chart in Figure 1 the second largest axis multiplicated with a factor of 0.85 was used to sort the aggregates in sieve classes according the the mesh size. This factor is needed because either the mesh size (edge of the "hole") or the diagonal is relevant to determine which grain would pass through which sieve, dependent on the shape of the grains. Therefore, this factor needs to lie between 1 and $1/\sqrt{2}$. For comparison the samples have been dissolved in HCl and sieved.

4. Summary

ME-CT can be used as a tool to non-destructively determine B:A ratio and granulometry of historic mortars. Especially fine grains are challenging due to the limited resolution of typical CTs (µm-range). However, it also allows for the investigation of mortars with calcite as aggregates that are problematic

4 Berg et al. 2019.

for acid digestion. Compared to PLM it has the advantage that the grains can be measured in 3D, and not only their cutting plane. Furthermore, the density of the binder can be determined with CT as well so that a gravimetric B:A ratio can be calculated. The potentials and limits of ME-CT for mortar analysis will be presented using a variety of reproduced and historic samples.

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Characterization of lime-based mortars from historic aqueducts in Cyprus

The study of traditional mortars is of interest to researchers working in the fields of civil engineering, materials science, architecture and archaeology. Due to their artificial cementitious nature, systematic studies on these composite materials usually showcase the technological achievements of past civilisations[1-2]. In the field of heritage conservation, interdisciplinary research on mortars is also essential for the design, production and application of compatible conservation materials. Past studies on historic and prehistoric composite materials worldwide have identified the use of various binders[3-4]. Lime, one of the most commonly used binders in construction, dates back to the Neolithic Era[5-6]. In Cyprus, the first use of lime plasters also dates back to the Neolithic period, while the widespread production of lime plasters became more common during the Chalcolithic period. During the Late Bronze Age, a significant development in lime mortar production occurred on the island, with the first intentional use of crushed brick-lime mortars in water-bearing structures, such as cisterns and aqueducts[7-8]. Even though a number of researchers have recently published results on mortars from Cyprus[9-10] their work has been limited either to specific historic or prehistoric periods or sites. Hence, comparisons in mortar production technology and development on the island among different sites and periods have not been possible.

This study presents preliminary findings from the analysis of seven (7) representative mortar samples collected from the remains of various aqueducts around Cyprus, dating back to different historic periods from the 4th to the 18th centuries. Sampling was carried out in collaboration with the Cyprus Department of Antiquities, in the framework of a larger research project aiming at gaining insight into the building technologies and raw materials used by past civilisations on the island. A detailed documentation of all specimens was conducted before the systematic and multiscale analysis of the mortars. Macroscopic and stereomicroscopic observations, along with other experimental analyses, were carried out to thoroughly characterize the samples in terms of their composition, properties and state of conservation. X-ray diffractometry (XRD) was used to identify the main crystalline mineral phases in both qualitative and quantitative terms. Combined differential thermal (DTA) and thermogravimetric (TG) analyses assessed the structurally bound water and classified the samples based on their hydraulicity. Mercury intrusion porosimetry (MIP) was employed to evaluate the pore structure and volume, as well as the average pore size. The macroscopic and stereomicroscopic observations revealed differences in texture, hardness and microstructure, likely related to the technology adopted for the production of these materials. In some

1 Miriello et al. 2010.
2 Genestar, Pons, Más 2006.
3 Wilkie and Dyer 2023.
4 Lancaster 2021.
5 Gourdin and Kingery 1975.
6 Kingery, Vandiver, Prickett 1988.
7 Theodoridou, Ioannou, Philokyprou 2013.
8 Philokyprou 2011.
9 Pizzo et al. 2024.
10 Philokyprou 2021.

samples, multiple layers were visible, with differences observed in the microstructure of the areas close to the exposed surface. Crushed ceramic fragments could be identified in almost all samples. The powder XRD results showed that calcite was the main mineral in all the samples, with quartz also present in considerable quantities. Plagioclase feldspars and actinolite were also commonly found, while gehlenite and hematite, characteristic of the presence of ceramic fragments, were present in most samples. These minerals confirm that crushed brick or ceramic was likely used throughout the periods of study for the production of the composites, in the absence of natural pozzolanas on the island, to enhance the performance of the hardened end-products by increasing their mechanical strength, adhesion and hydraulicity, thereby prolonging their longevity. Gypsum was detected in two specimens and could be attributed to secondary salt formation from atmospheric pollution. TG/DTA classified the mortars as weakly to eminently hydraulic. MIP results also indicated structural heterogeneity, reflecting possible variations in construction techniques over different time periods and the effects of weathering.

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Characterization of Lime Mortar from the Ming Dynasty Great Wall in Beijing, China: Composition, Microstructure, and Properties

1. Introduction

The Great Wall is a symbol of the Chinese nation and a world-renowned cultural heritage. Its main structure was initiated during the Ming Dynasty (1368-1644), with a total length of 8, 851.8 kilometers. It is one of the most iconic defensive engineering systems in human architectural history, showcasing the significant achievements of ancient China in materials science, construction technology, and other fields. The basic construction technique of the Ming Great Wall in the Beijing area involves tamping and stone masonry, with brickwork applied to the exterior of the tamped wall and traditional lime used as the binding material between the bricks and stones. Due to the influence of natural factors and human activities, the existing wall has experienced significant localized collapses and damage, with its overall preservation in a precarious state, facing imminent destruction. There is an urgent need to carry out protection, reinforcement, and restoration work on the remaining sections of the wall. Before implementing protective measures, a thorough scientific analysis of the original materials of the cultural heritage is necessary to determine their composition, structure, and properties. This is a crucial prerequisite for formulating a scientifically sound and reasonable preservation and restoration plan. This study is based on the research-oriented restoration project of the Jiankou section of the Ming Great Wall in Beijing. Representative mortar samples were selected and analyzed using modern detection techniques, including X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TG-DSC), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption, pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), and scanning electron microscopy (SEM). The aim is to explore the composition ratio and microstructure of the mortar samples, as well as to investigate the performance evolution mechanism of the mortar during the long-term carbonation process. This study provides a material foundation for the research-based restoration of the Great Wall in the Beijing area and contributes to the advancement of building heritage preservation materials.

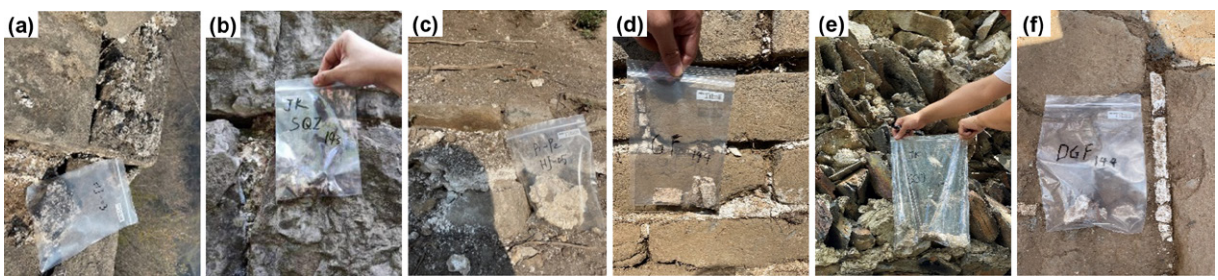

Figure 1. Schematic of mortar sample collection locations: (a) brick masonry, (b) stone masonry, (c) pavement masonry, (d) brick jointing, (e) stone jointing, (f) pavement jointing.

2. Sampling

Samples of mortar were collected from different parts of the Jiankou section of the Great Wall, as shown in Figure 1. The mortar was categorized into three types based on its location and purpose of use: brick masonry/jointing mortar, stone masonry/jointing mortar, and pavement masonry/jointing mortar. Due to prolonged exposure to the outdoors and direct contact with the soil, the surface of the mortar is covered with a layer of yellow soil particles.

3. Results and discussion

The XRF results show that the main components of the mortar samples from different locations are consistent, primarily consisting of Ca, Mg, and Si elements, with small amounts of Al, Fe, and S elements. The Mg content in all samples exceeds 10%, indicating that they are dolomitic lime, a type of air-hardening lime. The use of dolomitic lime has also been observed in studies of the Great Wall in areas such as Hebei and Beijing[1-2]. Additionally, all samples exhibit a high content of Si (greater than 6%), which may be related to the use of siliceous aggregates in the mortar.

FTIR spectra show distinct absorption peaks at 714 cm-1, 878 cm-1, 1430 cm-1, 1798 cm-1, and 2520 cm-1. Combined with the XRD results, it is evident that the inorganic components of the mortar are primarily in the form of calcite crystals (CaCO3). Py-GC/MS analysis indicates that the pyrolysis products of the mortar do not contain substances commonly found in the pyrolysis of polysaccharides, such as furfural, furfural ketone, or cyclopentanone, nor do they contain indole-type products typically generated by the pyrolysis of proteins. Combining this with the FTIR spectrum, it is clear that the lime mortar does not contain organic components such as glutinous rice branched starch or egg white additives.

From the perspective of pore structure characteristics, the pore sizes of the ancient mortar are concentrated in the range of 0.1-1 μm, which is an excellent performance for air-hardening lime. This is due to the carbonation process over time, during which the carbonation products effectively filled the pores, enhancing its density[3-4]. This increased density imparts the mortar with excellent freeze-thaw resistance and corrosion resistance. SEM images of the mortar revealed the microstructure of the inorganic components, where distinct columnar calcite crystals and some amorphous calcium carbonate were observed. The microstructure of the mortar from different locations was similar, with minor differences. In the brick masonry mortar, rod-like aragonite, cubic calcite, spherulitic aragonite, and amorphous calcium carbonate were observed. Additionally, small amounts of incompletely carbonated Ca(OH)2 plate-like crystals were found[5].

4. Conclusions

This study systematically analyzes the composition, microstructure, and macroscopic properties of the mortar from different sections of the Jiankou section of the Great Wall using techniques such as XRF, XRD, TG-DSC, FTIR, and SEM. The following main conclusions are drawn: (1) The binding material used in the Jiankou section of the Great Wall is pure dolomitic lime, without aggregate components. After long-term carbonation, the main inorganic component of the mortar is CaCO3 in the form of calcite crystals, with a content of approximately 80%. In addition, there are small amounts of MgCO3. The mortar does not contain organic components such as glutinous rice or egg white. (2) During the long-term carbonation process, the calcium carbonate generated by carbonation effectively fills the pores in the mortar, refining its pore structure. At the same time, the prolonged carbonation significantly regulates the growth process of calcium carbonate crystals formed through the carbonation of calcium hydroxide, limiting the

1 Liu et al. 2016.
2 Wei et al. 2020.
3 GZhou et al. 2021.
4 Rispoli et al. 2019.
5 Rispoli et al. 2019

crystallinity of calcite-type calcium carbonate, resulting in smaller calcium carbonate particle sizes and a denser mortar structure.

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Short-range Atomic Disorder of Carbonates and Silicates in Hydraulic Binders

1. Abstract

Pozzolanic reactions, fundamental to the development of hydraulic lime binders, involve the dissolution and recombination of amorphous aluminosilicate compounds with calcium hydroxide in an alkaline, lime-saturated aqueous solution. These reactions result in the formation of nanostructurally-polymerized, insoluble hydrates with excellent mechanical strength, low permeability, and high durability, even in underwater environments. However, understanding pozzolanic reactions remains challenging due to the amorphous and poorly crystalline nature of their products, which complicates their structural characterization. Consequently, various analytical methods are continually being developed to characterize the components of hydraulic lime binders. This study presents a novel approach to assess the short-range atomic disorder of the carbonate and silicate products of these binders. The approach includes combining Infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) to assess the local atomic environment, with X-ray diffraction (XRD) which allows decoupling the influence of crystalline structures from the aggregates from the amorphous products. FTIR helps evaluates the disorder of calcite crystallites based on the ν_2 and ν_4 vibrational modes, while silicate disorder is analyzed through peak asymmetry and full width at half maximum (FWHM). 29Si NMR shows the degrees of condensation of the SiO4 tetrahedra, differentiating between monomeric, dimeric, chain or ring, sheet-like, or 3D polymer structures (annotated as Q0-4). By combining the two short-range atomic order assessments, we show a link between highly disordered materials, associated with products of pozzolanic reactions, in the two methods. We exclude the influence of phases from different aggregates that are found in the binder: namely pozzolanic materials at Caesarea (Secco et al. 2022), organic combustible remains mixed with cocciopesto at Nora (Secco et al. 2020), natural hydraulic mortars from the Charles Bridge at Prague (Kozlovcev and Přikryl 2015), in comparison to modern cements. These sites span the Mediterranean, from prehistory - where no evidence for hydraulicity is found in Middle Bronze Age Kabri (Goshen et al. 2017) and Neolithic Yiftahel (Poduska et al. 2012), through the Iron Age at Tel es-Safi/Gath (Regev et al. 2010), Roman and medieval periods, representing different environments and technologies.

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Applicability of Hygric Tests to Small Mortar Samples from Historical Buildings in Ukraine

1. Introduction

The characterization of historic masonry mortars presents significant challenges due to the difficulty in extracting standardized samples and the inherent heterogeneity of the material. Variability in composition, degradation over time, and limited sample sizes often hinder the applicability of standard test methods. This study investigates the feasibility of using hygric characterization tests commonly applied to porous building materials on small mortar samples. The research focuses on mortar specimens extracted from two historical buildings in Ukraine, aiming to evaluate their capillary absorption coefficient and total water absorption capacity. The results contribute to the optimization of conservation strategies by enabling moisture-related assessments on limited material volumes.

2. Materials and methods

2.1 Sample collection and preparation

Mortar specimens were extracted from masonry bed joints of two historic buildings in Ukraine, namely the Land Management Building of the Lviv National University of Environmental Management in Dubliany, dating to the late 19th century, and the Taras Shevchenko Regional Academic Music and Drama Theatre in Chernihiv, built in the mid-20th century. These buildings were selected for their historical value and distinct construction typologies, allowing for a comparative assessment of mortar properties across different historical periods and material compositions.

Together with the mortar specimens, full bricks were collected from both sites to provide contextual information on the masonry materials. Given the fragility and small dimensions of the extracted mortar specimens, adjustments to standard testing protocols were necessary to ensure reliable characterization of their moisture transport properties.

2.2 Hygric tests on small samples

To evaluate the moisture transport properties of the mortar samples, the study focused on two key paraTo evaluate the moisture transport properties of the mortar samples, the study focused on two key parameters, namely total water absorption and capillary absorption. Both tests were adapted from standard procedures to accommodate the reduced size and irregular geometry of the specimens. The immersion test was based on the procedure developed by Plattner et al.[1], in which the sample is fully submerged in water and its mass increase is recorded over time. In the adapted setup, samples were suspended from a high-precision digital balance, and mass measurements were logged automatically to minimise handling and improve repeatability. Similarly, the capillary absorption test followed the principles of the standard water uptake method to determine the capillary absorption coefficient, Aw, but the setup was adjusted to allow only the lower portion of the specimen to remain in contact with water, while mass gain was mon-

1 Plattner et al. 2012.

itored under the same automated conditions. Both procedures share the same equipment and general configuration, differing only in the degree of water exposure.
Due to the impossibility of extracting standardised specimens from the historic mortar joints, direct validation of the procedures on mortar was not feasible. However, full bricks collected from the same buildings provided a means to test the adapted methods on a comparable porous material. These bricks were first tested in standard dimensions, then reduced to smaller sizes and subjected to the same modified procedures. The consistency of results across both scales helped assess the influence of specimen size on measurement outcomes and confirmed the reliability of the adapted setup. This approach provided a reference framework to interpret the results obtained from mortar samples under the same test conditions.
Finally, given the limitations associated with small specimen size and the need for non-invasive techniques in heritage contexts, infrared thermography was also considered as a complementary method for capturing moisture ingress. This technique, as proposed by Marynowicz and Kucharczyk[2], offers a non-contact means of tracking capillary rise through thermal imaging.

3. Results and discussion

3.1 Total water absorption of small samples

The adapted immersion test for smaller mortar samples was used to determine total water absorption values. The application of this method to non-standardized specimens requires adjustments to address potential size-related variations in absorption behaviour. The comparison with brick reference samples provides insights into the feasibility of applying this test to smaller mortar specimens, particularly in terms of measurement consistency and reproducibility. Observations regarding mortar size, porosity, and potential deviations from standard test expectations can help assess the suitability of this approach for other historical materials.

3.2 Capillary absorption of small samples

The feasibility of capillary absorption tests for small mortar samples was explored by adapting standard gravimetric capillary rise methods. While these tests can provide meaningful data, preliminary observations indicate that a minimum sample mass and surface area are necessary to obtain reliable absorption curves. Inconsistencies may arise due to mortar inhomogeneity, presence of cracks, or variations in pore structure.
Infrared thermography was considered as a potential non-contact alternative for evaluating capillary absorption. While this technique has been successfully applied to larger masonry elements, its effectiveness for small-scale specimens remains uncertain. The study aims to determine whether spatial resolution limitations or emissivity variations pose significant challenges when working with non-standardized mortar samples.

3.3 Challenges and Considerations

The study highlights several challenges associated with the hygric characterization of small mortar specimens, particularly concerning sample size constraints, material heterogeneity, and testing precision. One of the key limitations is the increased surface-to-volume ratio of small samples, which can affect absorption kinetics and complicate direct comparisons with larger, standardized reference specimens.
Additionally, microstructural variations and degradation in historical mortars introduce further uncertainties in moisture transport. Surface roughness and pore structure irregularities influence both capillary absorption and total water uptake, requiring careful interpretation of results. While methodological adaptations have been implemented to minimize handling errors and improve measurement consistency, the study acknowledges that certain limitations remain when applying standard hygric tests to fragmented or small-scale heritage materials.

2 Marynowicz and Kucharczyk 2021.

Beyond gravimetric techniques, non-destructive testing methods, such as infrared thermography, are being explored as potential complementary tools for assessing moisture behaviour in historic mortars. However, their application to small specimens presents challenges related to resolution, sensitivity, and data correlation with gravimetric findings. Further refinement of these approaches will be necessary to enhance their reliability in heritage conservation.

4. Conclusions

This study examines the applicability of hygric characterization methods commonly used for porous building materials to small mortar samples extracted from historic structures. While standard methodologies were adapted to accommodate size constraints and material fragility, certain limitations related to minimum sample dimensions were observed. The evaluation of total water absorption and capillary absorption provided insights into the feasibility of using these techniques on non-standardized mortar specimens, while comparisons with brick reference samples helped assess measurement consistency. The findings contribute to a better understanding of moisture transport properties in historic mortars, offering potential improvements in conservation assessment strategies. However, additional refinements are needed to address variability in porosity, degradation, and sample heterogeneity.

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CARLOS RODRÍGUEZ-NAVARRO

Ultrastructural and compositional analysis of ancient Roman mortars and their novel biomimetic counterparts

1. Background

Ancient civilizations implemented the use of natural additives (e.g., milk, sticky rice, oils, animal fat, or plant extracts) in mortars and plasters to modify their final properties. Such materials have displayed unmatched durability. It has been previously confirmed[1] that organics provide improved physical-chemical properties, similar to natural biomacromolecules in biominerals, via lattice strain and microstrain fluctuations that can be measured by in situ thermal synchrotron high-resolution X-ray diffraction (HRXRD)[2]. This is so because, upon slaking of CaO to form Ca(OH)2 (portlandite), organics are incorporated into the calcite cement formed after carbonation, as it happens in biominerals, leading to biomimetic CaCO3 cement in lime mortars and plasters, with improved strength and toughness similar to those of carbonate biominerals. Recent high-resolution transmission electron microscopy (HRTEM) and synchrotron HRXRD work on ancient Maya lime mortars and plasters as well as their modern replicas showed organics incorporation in the lattice of calcite resulting in nano-structural changes that help explain the high durability of such plasters[3]. Our preliminary synchrotron HRXRD study of ancient Roman mortars and plasters also shows lattice distortions and peak broadening in the calcite binder, suggesting the presence of occluded organics, and enabling the differentiation between geologic calcite, added as aggregate, and the calcite formed after the carbonation of the binder based on the structural differences[4].

2. Objectives

Our on-going research aims at further understanding the role of different organic additives in the structural properties of both ancient and modern biomimetic lime mortars and plasters. The reverse engineering study on the effects on lattice distortion and microstrain fluctuations of calcite in lime mortar replicas using natural and synthetic organic additives will allow us to: (i) disclose the mechanisms by which natural and synthetic organic molecules are incorporated into the calcite lattice during the early stages of slaked lime carbonation, forming biomimetic calcite structures; (ii) understand the organics-induced microstructural effects and their influence on the micro- and macroscopic properties of historical lime mortars; (iii) design novel biomimetic lime-based conservation materials with improved chemical and mechanical properties. The expected results could help to unveil the secrets of the high-quality building technology developed by the ancient Roman civilization. Also, they could have a significant impact on the development of optimized lime-based conservation mortars, as well as low C footprint sustainable building materials.

1 Rodríguez-Navarro 2017.
2 Pokroy 2006.
3 Rodríguez Navarro 2023.
4 Atiénzar 2024.

3. Materials and methods

A set of 20 historic lime mortars samples, including opus signinum, opus caementicium, stuccoes with paint layers, and mosaic beddings, were obtained from a recently discovered ancient Roman (IV-V c. CE) Villa located in Salar (Granada, Spain) that stands out for its excellent state of conservation (Fig.1, left). In addition, different replica plasters were prepared mixing hydrated lime with water in a 1:1 (wt/wt) ratio, in the absence (control) and presence of different organic additives (proteins and amino acids) and subjected to a 4-month carbonation process in air at 70% RH and room T. HRXRD was performed at the CRYSTAL beamline of the Soleil synchrotron (Paris, France). Synchrotron energy and top-quality monochromators and detectors were essential to obtain diffraction patterns at T ranging from 25 to 400 °C with sufficient intensity and angular resolution to disclose the intracrystalline incorporation of organic molecules and their effect on lattice strain (~10-3-10-4) and microstrain of calcite crystals, as the small shifts in Bragg peaks compared to purely inorganic calcite are undetectable with standard low-resolution Cu-Kα X-ray diffractometers. Diffraction profiles were fitted using the Rietveld method, for unit cell refinement, and lattice strain determination. Micro-strain and crystallite size were calculated using the Williamson-Hall plot. Additional nano/microstructural and compositional characterization was carried out using Fourier transform infrared spectroscopy (FTIR), thermogravimetry and differential scanning calorimetry (TGA/DSC), and high-resolution scanning/transmission electron microscopy (SEM, TEM) coupled with energy dispersive X-ray (EDX) analysis.

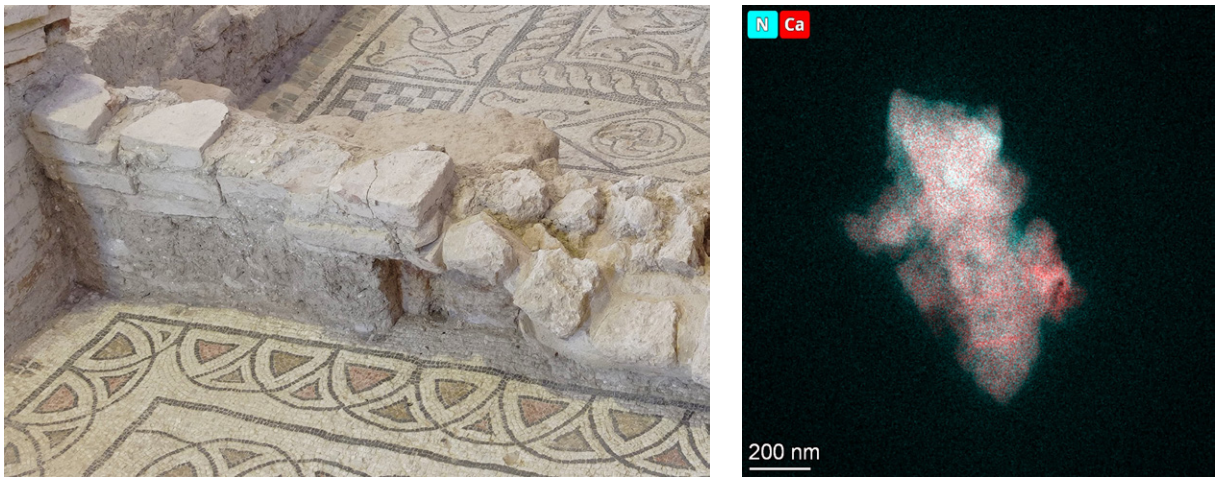

Figure 1. General view of a masonry wall between floor mosaics containing lime mortars in Salar, Granada (left). TEM-EDX mapping of calcite in a replica plaster showing N (blue) concentration from L-aspartic acid at the particle edges as well as in the bulk (right)

4. Results and Discussion

The presence of organics in historic mortars was detected by FTIR and TGA/DSC analyses and confirmed through HRXRD thermal analysis and HRTEM-EDX. HRXRD patterns showed a shift of the Bragg peaks related to a larger unit cell and greater microstrain due to the occlusion of intracrystalline organics. Such a shift disappeared after annealing, matching the parameters of geological calcite. HRTEM revealed amorphous regions within homogeneous areas of crystalline calcite, also suggesting the presence of occluded organics. EDX compositional mapping (Fig.1, right) confirmed the presence of elements, such as N and P (not pictured), believed to be part of the organic fraction of the samples (both in historic mortars/plasters and replicas with added proteins/amino acids). These elements appear as a veil around the nanoparticles examined, suggesting that the organic material is adsorbed on the surface. Additional profile measurements allowed a more detailed semi-quantitative analysis, which helped to confirm the presence of occluded organics inside the calcite particles and elucidate the mechanism by which organic matter is adsorbed and occluded in the crystal structure. The fact that the same structural characteristics and modifications were found in the carbonated hydrated lime replicas and the ancient lime mortar samples from

the Roman Villa de Salar shows that, very likely, the Roman masons purposedly added the organics (likely proteinaceous additives) to their mortar and plaster mixes to improve their properties and performance. Our preliminary results prove the use of organic additives in historic lime mortars and have important implications for the study of ancient building technology and the development of state-of-the-art lime-based materials for conservation purposes.

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Four different mortars in a Medieval church: surface strength, mineralogy and compatibility

1. Introdution

The present study focuses on the use and analyses of various types of mortars in a Medieval ruined church in West Central Hungary. The church is located near the largest lake of Central Europe, Lake Balaton. It was constructed in the 13th century. During its stormy history it was rebuilt in several periods using additional lithotypes and various types of mortars. The paper outlines the physical and textural properties, as well as mineralogical composition of mortars and emphasize the different use of renders and compatibility issues with various lithotypes. The weathering related alterations of different mortars are also addressed.

2. Materials and Methods

The complexity of the material use in this church is well reflected in the wide range of lithologies used as ashlars and carved stones. Several types of bricks and 4 types of mortars were also found. 13 different lithotypes were identified including red sandstone (Permian), grey sandstone (Miocene) various cemented limestone, including bioclastic, cemented and micro-crystalline (Mesozoic), porous limestone (Miocene), travertine (Pleistocene), basalt and basalt tuff (Pliocene). The mortars also show great varieties, since four different types were recorded. Two types of Medieval lime based mortar, one later repair mortar and one twenties century Portland cement containing mortar. The on-site tests included the description of mortars, surface strength measurements using Duroskop and moisture content analyses. Samples were taken for laboratory testing. Physical parameters were measured. Textural- and mineralogical/chemical compositional analyses were made by optical microscopy and by SEM-BSE, SEM-EDX.

3. Results and Discussion

The first type of Medieval mortar is yellowish lime based mortar with basalt tuff, brick aggregates. The aggregates are fairly rounded. It is considered the oldest mortar type used as masonry mortar in the first church (Figure 1). Despite is age it is in good condition with relatively high surface strength. Namely its mean Duroskop rebound value is 21. The second Medieval mortar is also lime based with fine aggregates of porous limestone and lime lumps. Its surface strength is even higher that that of the mortar 1 type, with a mean Duroscop rebound value of 26. Third mortar type is beige – grey with a few quartz grains as aggregates and a few limestone particles. It is considered as a repair mortar with post Medieval period. The surface strength is less than the Medieval ones with a mean rebound value of 19. The latest mortar is a 20th century grey one with Portland cement. It was used in the 'restoration' works in late 1950'ies. It has a low porosity and high surface strength of 33 Duroskop rebound value. It contains significant amount of rounded quartz grains and small amounts of fine black basalt grains. The moisture content measurements clearly reflects the open porosity of tested mortars. The Medieval mortars show mineralogical alterations. Gypsum crystals were detected at the surface of the lime-based mortars reflecting the interaction of air pollutants and calcite, representing a secondary mineral phase. Despite this alteration these mortars

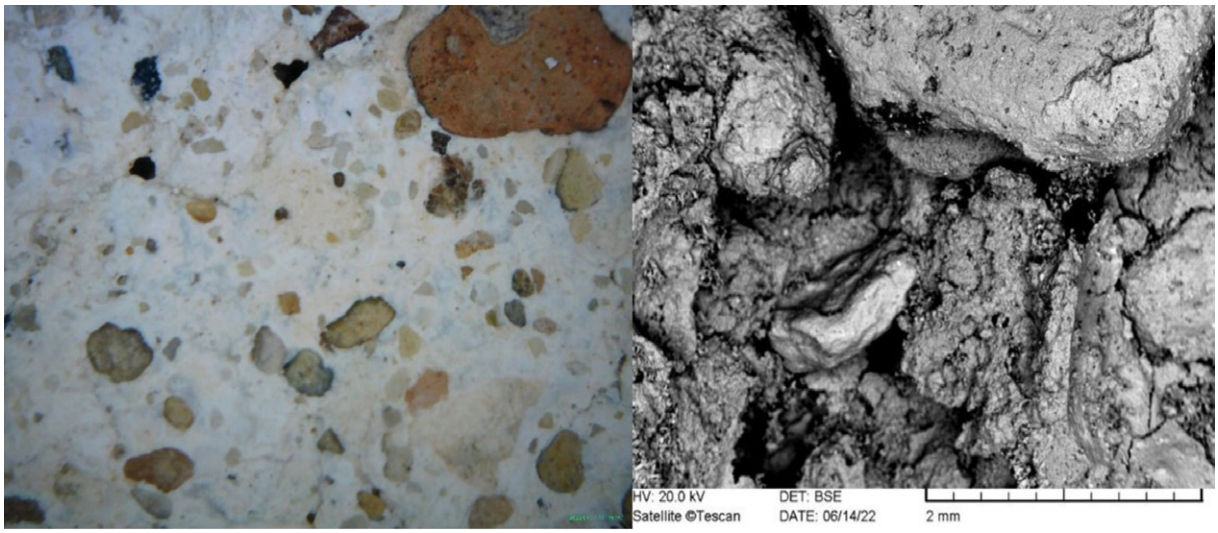

Figure 1. Stereomicroscopic and BSE image of Medieval lime mortar

are still in good conditions unless they were covered with the latest 'repair' mortars containing portland cement. In that case the historic mortars suffered frost damage. The post Medieval third type of repair mortar show alterations such as powdering. The portland cement containing latest mortar has several micro-cracks and it shows intense spalling at many surfaces.

4. Conclusions

The Medieval lime-base mortar is compatible for all 13 lithotypes of the Medieval ruined church. It is more durable than the later mortars used in the restoration works. The Portland cement containing grey mortar has the highest surface strength, but its low porosity does not allow the water vapour transport and if it is used to cover the historic mortar surface it accelerates the decay of lime mortars. The most severe deterioration was observed at wall sections were the 20th century portland cement containing mortar was used to cover the slightly weathered stone surfaces.

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Integrated SR-μXRPD and FPA-FTIR Techniques for High-Resolution Natural Hydraulic Binder Analysis in Historic Mortars

1. Aim of research

Ancient hydraulic mortars were made using natural hydraulic lime binders or mixing air hardening binders with pozzolanic materials. The setting and hardening process of these mortars is complex, as is their composition, which varies depending on the raw materials, the environment of preservation, and the age of the material. Numerous analytical techniques are used to evaluate the composition of each component and to analyse the compounds that develop during setting and hardening of these mortars[1].

Our research focuses on analysing the binder of natural hydraulic mortars obtained by firing marly limestone, which is naturally rich in clay minerals. In natural hydraulic binders, after setting, the phases of non-hydrated clinker, calcite, calcium-modified silica gel and aluminium oxide stabilize (resulting from the presence of non-hydrated clinker, hydrated calcium silicates, and calcium aluminates, CSH and CAH)1. In addition to calcite, aragonite and vaterite are also commonly found. The carbonation of Ca(OH)2 has as its first step the transformation into amorphous calcium carbonate (ACC), then it is transformed into aragonite (arg), vaterite (vtr) or calcite (cal)[2]. The ACC is unstable and crystallizes into CaCO3 (arg, vtr or cal), with calcite being the most stable form[3]. In this study, we investigate the distribution of calcium carbonate polymorphs (calcite, aragonite, and vaterite) and calcium-aluminium silicate hydrate (CASH) phases within mortar samples from historical Florentine buildings.

2. Materials and methods

Binder from mortar samples belonging to Giotto's Bell Tower was characterized using a combination of conventional and advanced techniques[4]. Conventional techniques included X-ray Powder Diffraction (XRPD) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), which provided identification of mineral phases and functional groups. Advanced techniques included Synchrotron Radiation micro-X-ray Powder Diffraction (SR-μXRPD) and Focal Plane Array-Fourier Transform Infrared Spectroscopy (FPA-FTIR), which enabled high-resolution imaging of both crystalline and amorphous phases, offering a more comprehensive understanding of the mortar's composition and microstructure. The combination of tailored sample preparation and the high spatial resolution of advanced techniques enabled the acquisition of highly resolved, high-quality chemical and mineralogical images from the same sample portions.

1 Parra-Fernández et al. 2024.
2 Ogino, Suzuki and Sawada 1987.
3 Rodriguez-Navarro et al. 2015.
4 Cantisani et al. 2021.

3. Results and discussion

Preliminary XRPD analysis onof the binder identifiedindicated the presence of calcite, aragonite, vaterite, and CASH phases. XRPD suggested the presence of calcium carbonate phases alsoeven in lumps, ATR-FTIR suggestedindicated the additional presence of amorphous silicates, that was detected as a broad band centred at 1100 cm−1. ATR-FTIR spectra detected the presence of calcium carbonate and silicate components, although the vaterite peaks were often masked by silicate interference. ATR-FTIR analysis does not detect the presence of organic phases.

Calcium carbonate and silicate compounds were further identified and spatially mapped throughby FPA-FTIR and SR-µXRPD techniques allowed for, allowing detailed spatial analysis of these phases (Figure 1).

In GBT binder and lump calciteCalcite, aragonite, vaterite, and CASH phases were detected through SR-µXRPD analysis, while calcite/vaterite, aragonite and the amorphous and crystalline silicate phases were characterized using FPA-FTIR. TheseThe latter were observed to be located in the same regions, particularlyespecially in association with aragonite. Relativevaterite. Their relative distribution may indicatesuggest that silicates are the phases that stabilise aragonitevaterite and slow the kinetics of conversion to calcite (REF). Vaterite is only present to a small extent, thedown its transformation into calcite. The point at which itwhere the vaterite content is higher corresponds to a higher amount of CASH and is surrounded by calcite and aragonite. Aragonite is present along with CASH, and is absent where the calcite. It can be deduced that the contribution of vaterite is often associated with calcite, which is confirmed by and vaterite are mapped. This confirms the transformation sequence ACC-arg-vtr-cal2.

The results suggestindicate that the presence of CASH and amorphous silicate phases maycan stabilize aragonite and vaterite and delay itstheir transformation into calcite. Furthermore, the coexistence of variousdifferent phases indicates a complex interaction between calcium carbonate and silicate components.

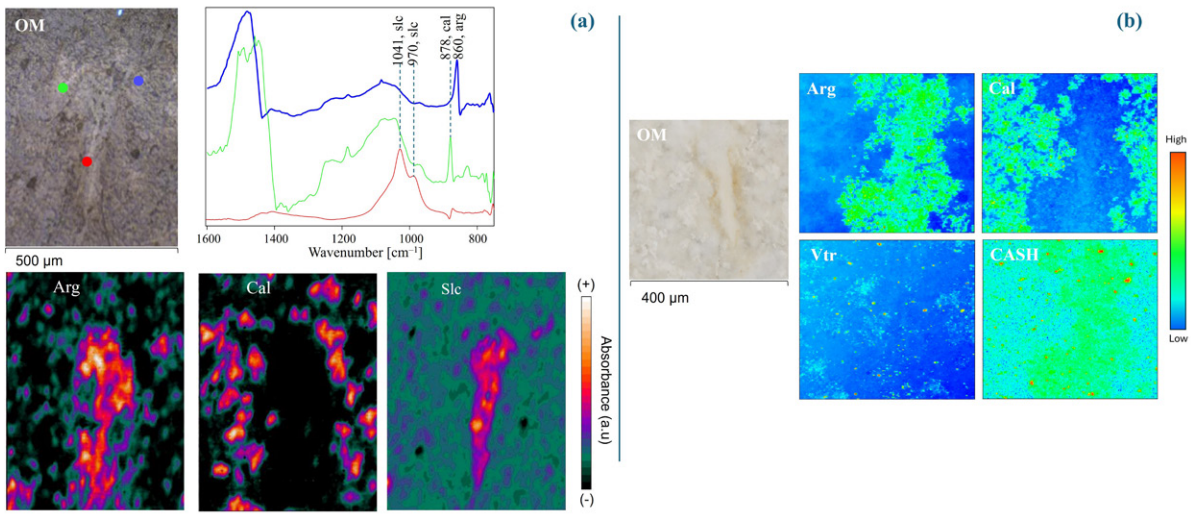

Figure 1. Analysis of binder with FPA-FTIR and SR-µXRPD. a) FPA-FTIR: Investigated area using OM (3x4 frame), point analysis, and absorbance spectra. Chemical distribution maps: arg, cal/vtr and slc. b) SR-µXRPD: Investigated area using OM (ROI ~400 × 360 µm2) and distribution maps: arg, cal, vtr, and CASH

Conclusion

The combined application of SR-µXRPD and FPA-FTIR has proven to be effective in distinguishing calcium carbonate polymorphs and associated silicate phases within ancient mortars. These analyses allowed us to distinguish different chemical and mineralogical species based on their distinct spectral and diffraction patterns and to generate high-spatial-resolution maps of either crystalline (SR-µXRPD) or amorphous/crystalline (FPA-FTIR) compounds. The data suggest that the presence of amorphous silicates may

hinder the carbonation process, leading to the coexistence of metastable calcium carbonate polymorphs, such as aragonite and vaterite, alongside calcite.
For the first time, in this study SR-μXRPD and FPA-FTIR were applied to investigate ancient mortars, demonstrating the complementarity of these high-resolution imaging techniques which was necessary to provide answers to the controversial aspects of the stability of calcium carbonate polymorphs and of crystalline and amorphous calcium silicate in the binder of ancient mortars. These results are fundamental for understanding the ancient production technologies and the chemical transformations that may confer hydraulicity and durability to these ancient materials.

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Luminescence of secondary crystallisation phases in archaeological lime mortars: characterisation and identification

In building archaeology, lime mortar analyses provide essential information for interpreting construction methods, differentiating construction phases and understanding the evolution of buildings. When mortar is applied, it hardens by incorporating CO2 from the atmosphere, making carbon-14 dating possible. However, direct radiocarbon dating of mortar remains a challenge, due to the presence of other carbonates, such as geological carbonates or secondary calcite crystallisations. Indeed, the presence of the latter leads to a bias in dating. It has been shown in recent years that characterisation of the material is a prerequisite for ensuring the reliability of the age obtained[1]. The main aim of this characterisation is to identify the different calcium carbonates, and make it possible to separate the binder from the carbonates that distort the dating. We will demonstrate the use of UV irradiation for the identification of secondary crystallisation zones on the surface of several samples (Cluny abbey, St-Ferreol church, Brevenne aqueduct). These results will be compared with reference techniques (Scanning Electron Microscopy, Raman, Fourier transform infrared spectroscopy).
However, the origin of secondary crystallisation remains debated. One of the main hypotheses concerns the dissolution of lime mortar by run-off water. This hypothesis is supported by the observation of photoluminescence in recrystallised regions, similar to that observed in speleothems, where it is attributed to the presence of fulvic and humic acids resulting from the decomposition of organic matter in soil, transportation by run-off water and fixation in carbonate crystallization[2].

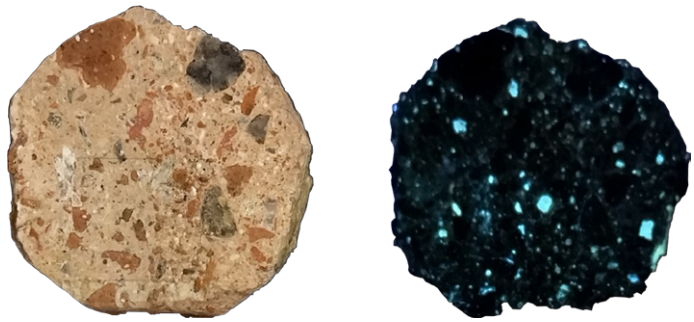

Figure 1. Optical image and photoluminescence UV-365nm image of lime mortar from Brevenne aqueduct

Secondary crystallisation were sorted by hand under UV light, using the presence of photoluminescence as a criterion. To extract potential humic and fulvic acids (from decomposing plant matter), these crystals were dissolved in acid and the extract was then subjected to solid phase extraction. The samples were measured by mass spectrometry (negative mode ESI on FT-ICR MS 7T 2XR SolariX - Bruker). At the same

1 Urbanová et al. 2020.
2 Shopov 2004.

time, thin sections and raw samples were imaged by LDI-MS (Laser Desorption Ionisation-Mass Spectrometry).
The identification of the families of compounds present in the extraction product produced some very interesting results, showing for examples humic acid, lipids, … in these calcite crystals. These results also show the relevance of using UV fluorescence to evaluate the potentiality of mortars for 14C dating.

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Image processing and analysis in archaeometry: unveiling roman mortars from the thermal baths of teate marrucinorum (Chieti, Italy)

1. Introduction

The archaeometric characterization of geomaterials and their artificial counterparts used in antiquity can be constrained via complementary mineralogical, geochemical, and textural analyses. This is crucial for understanding raw material provenance, reconstructing ancient building techniques, and assessing their durability. Morphotextural studies are commonly performed in the 2D domain on polished slabs and thin sections, to determine abundance, dimensions, number of crystals/clasts per surface, size frequencies, shapes, orientations, etc. of crystalline vs non-crystalline phases, voids, and particles[1]. Similarly, morphotextural investigations can be performed via 3D images and their analysis, enlarging and detailing further parameters, i.e. volume fractions, specific surface, connectivity and anisotropy. Here, we focus on the combined application of 2D and 3D image processing and analysis techniques on mortars from the public thermal complex of Teate Marrucinorum (Chieti, Italy, Figure 1) to obtain a detailed textural profile of these ancient samples.

2. The thermae of Teate Marrucinorum and their cisterns complex

Teate Marrucinorum, in the modern city of Chieti in the Abruzzo region (Italy), was an important municipium during Roman times. This is evidenced by the numerous archaeological sites as the Roman theatre, the Civitella's amphitheatre, the sacred temples area, and thermal baths complex (Figure 1a). The influence of Teate Marrucinorum in antiquity is further demonstrated by the refined decorations of the public thermal baths (1st–2nd century AD), having ornamental wall panels and pilasters and an intricate mosaic floor[2]. A large cistern system nearby fed the thermae; it consists of nine vaulted rooms powered by natural occurring water led by Roman canalization.

3. Imaging techniques and image analysis

Two horizontal core samples were extracted from the internal walls of the cisterns, sampling from the outermost to the innermost layers. The portions of these semi-cylindrical specimens (total lengths of 30 to 15 cm and diameter of 6 cm, Figure 1b) were first imaged in the 2D domain via a High-Resolution Scanner (HRS, Figure 2). Representative thin sections were obtained coaxial to the thickness and then analysed with Transmission Optical Microscope (TOM) and Scanning Electron Microscope (SEM, Figure 2) to investigate morphotextural attributes of phases from the largest to the tiniest[3]. The outermost half-portions of these specimens were furthermore investigated applying the non-destructive technique of X-ray computed microtomography (µ-CT, Figure 2) using an EASYTOM XL230 X-ray µ-CT system (RX Solutions, France). This 2D + 3D approach allows a complete characterization of the pores, aggregate

1 Higgins 2006.
2 Agostini et al. 2002.
3 Radica et al. 2024.

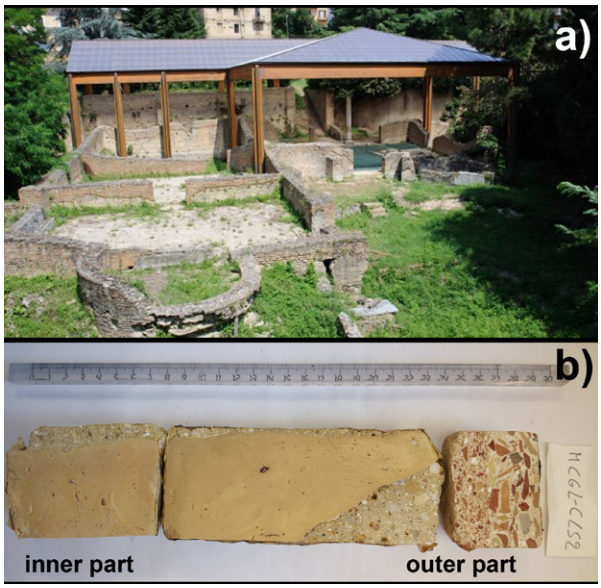

Figure 1. a) View of the archaeological site of the Roman thermal baths of Teate Marrucinorum (Chieti, Italy). b) Photograph of the polished cut half-portion of the core sample taken from the cistern's walls of the thermae.

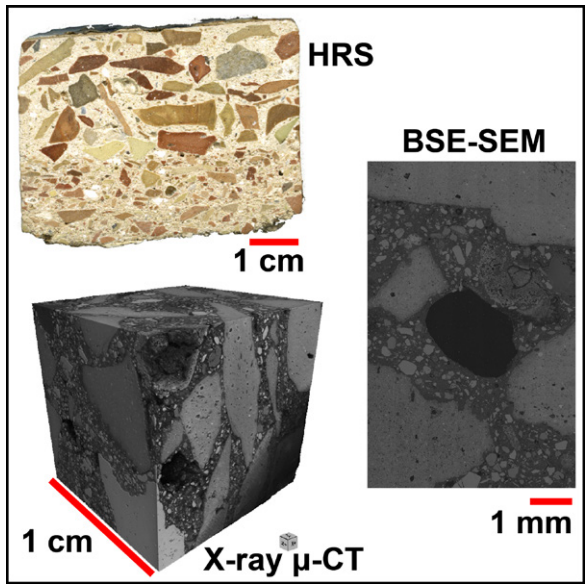

Figure 2. Imaging methods adopted (here MCGL-CLS-2A sample). From the top to the bottom: HRS (high-resolution scanner) of the outermost part of the core sample; BSE-SEM (scanning electron microscope with back-scattered electrons) of a portion of the thin section; volume rendering of a volume of interest obtained by X-ray µ-CT (X-ray computed microtomography).

phases and binder matrix, quantifying the cement-to-aggregate ratio, as well as the orientation, shape and size distribution of pores and aggregates; remarkably, also the morphotextural attributes of different types of aggregates can be quantified. These outcomes furnish new insights on the production techniques used in ancient times and on the state of preservation of this archaeological heritage site.

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Preliminary archaeometric analyses on artificial conglomerate blocks: the case of the Maconi tower, Siena (Italy)

1. Introduction

The Maconi tower[1] belongs to one of the oldest and most important lineages of Siena, whose exponents reached, between the 12th and 13th centuries, apical roles in the institutional and political life of the city. The reference points of the family were the palace and the tower, located in a dominant position with respect to the Francigena and the Piazza del Campo and at the center of a vast real estate heritage. The structure of the tower, only partially preserved, is characterized by a very particular construction technique: together with cavernous limestone blocks, there are reused Roman materials and large blocks of artificial conglomerate, whose origin, construction procedure and installation are not currently known. The latter have a regular parallelepiped shape and are made up of angular stone elements immersed in mortar. The aim of this study is to understand the methods of production and use of these particular blocks, attested exclusively in some structures, mainly towers, of the 12th-13th centuries.

2. Mortar samples and methods for their characterization

The methodology adopted for the archaeometric analysis and diagnostics of the state of conservation of the numerous artificial conglomerate blocks present on both the external and internal facades of the Maconi tower is based on a multidisciplinary approach that combines non-invasive survey techniques and laboratory analytical investigations. In particular, the study was conducted using a three-dimensional photogrammetric survey with LiDAR (Light Detection and Ranging) technology, aimed at detailed mapping of the surfaces of the blocks, as well as through the collection of representative samples. The analyses carried out include macroscopic observations for the determination of color, X-ray diffraction (XRD) for the determination of crystalline phases and observations under a polarizing optical microscope for mineralogical-petrographic characterization.

2.1 Study of the state of conservation

For the non-invasive study of the state of conservation, a 3D photogrammetric and LiDAR survey of the internal walls of the masonry structure was carried out, with manual segmentation of the virtual models of the visible surfaces of the artificial drafts and the classification of the different components using the Blender software application, which provided details on the geometry of the stone elements and any anomalies present in them.

2.2 Sample collection

Representative samples were taken from the artificial conglomerate blocks present in the internal north-east and south-east walls of the tower.

1 Bruttini 2021.

3. Results and discussion

The analysis of the state of conservation has revealed that the external elements show differential erosion phenomena, caused by atmospheric agents and the presence of a slightly protruding gutter; on them it is possible to recognize a biological colonization, which favors superficial degradation, with detachment of the mortar that joins the stone elements. Despite this, the state of conservation is overall good although ordinary maintenance is required. As regards the internal elements, the state of conservation is excellent, with the presence of dust accumulation on the surface of the blocks due to lack of maintenance over time.

3.1 Mineralogical-petrographic characterization

Samples were collected consisting of mortar and a few carbonate stone clasts, consisting of various fragments, the largest of which was approximately 30.00 mm. Their appearance was fine and homogeneous, with a tenacious consistency, with numerous white lumps (H10YR-V8-C1) of millimetric size and various clasts of variable size between 3.00 and 5.00 mm. The overall color was light gray (H10YR-V7-C2). Thin sections were prepared and the mineralogical-petrographic analysis[2] showed that the binder has an inhomogeneous structure at the mesoscopic level and a micritic texture at the microscopic level, resulting in classification as air lime. Millimeter-sized lumps with a micritic texture were identified. The aggregate shows a classification degree ranging from moderate to poor, with spherical clasts of low grade and rounding ranging from sub-angular to angular. The grain size ranges from 100 µm to 6200 µm, with a prevalence between 240 µm and 600 µm, including fragments of Pliocene sandstone, clay-cement sandstone, bricks and shales. The mortar is mainly composed of single crystals and polycrystalline aggregates of quartz, fragments of micritic and spathic calcite, feldspar, white and black mica and micro-nano crystalline aggregates of iron oxides. The mortar mix is lean, well amalgamated and relatively well sorted, with a binder-aggregate ratio of about 1:2. Finally, secondary processes and degradation products were detected, including the presence of gypsum crystals in the vicinity of a brick clast[3].

4. Conclusions

The preliminary archaeometric analyses conducted on the artificial conglomerate blocks of the Maconi tower have highlighted a good general state of conservation of the material, suggesting an excellent construction system. It is therefore proposed to reproduce them in the laboratory with characteristics similar to the original ones to understand the construction techniques and imagine their reuse in construction. The mineralogical-petrographic characterization has revealed the presence, within the cement matrix, of

Figure 1. Artificial conglomerate blocks from the Maconi tower, left, and image of the mortar obtained by thin-section polarized light microscopy, right.

2 Scala, Gabbrielli, Giamello, & Mugnaini 2021.
3 Pecchioni, Fratini, & Cantisani 2014.

an aggregate composed of minerals and lithic fragments compatible with the local geology, indicating the use of raw materials found in the vicinity of the city of Siena.

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Non-destructive methods for the characterization of historical building materials from the ottoman era: the case of the houses of the Kasbah of Algiers

1. Abstract

The characterization of building materials is a fundamental aspect, both for assessing the structural performance of historic buildings and for their structural upgrading.

The restoration of historic buildings requires a thorough understanding of the materials they are made of. While destructive testing is preferred for the characterization of historic materials due to the accuracy of the results, [1] [2], in situ sampling is challenging, particularly for listed or protected historic buildings, where the number of samples is generally limited. [3] [4]. Through the research presented in this article, we illustrate the characterization process of a selection of historic samples extracted from the Kasbah of Algiers, a UNESCO World Heritage Site since 1992, using semi-destructive and non-destructive testing.

The old medina is a complete urban complex which has various architectural typologies including houses, mosques, mausoleums, baths, shops, etc. It represents the tangible manifestation of a unique local know-how of master builders resulting from the Algiers way of life of yesteryear allowing the emergence of an exceptional Vernacular Architecture.

Semi-destructive testing was performed on a masonry wall fragment and Thuya wood (Tetraclinis articulata) using two distinct methods. The first method consists of estimating the strength of the lime and clay mortar in the masonry joints using a Type N penetrometer, (Figure 1), designed for low-strength mortars. [5] [6]. The second method assesses the density and fiber homogeneity of three different conservation states of Thuya samples. (Figure 2). In addition, the device identified areas with insufficient structural integrity, such as cracks. An IML-RESIF400-S resistograph recodes changes in torque strength using a stylus on graph paper.

Non-destructive testing was performed on clay bricks and cedarThuya wood using two distinct methods. The first involves estimating the moisture content of three Thuja wood samples using a Tramex MEP moisture sensor. The second method involves determining the density and homogeneity of the terracotta bricks by emitting ultrasonic waves using a Controls ultrasonic pulse analyzeranalyser. The characterization of the Thuja wood provides important information regarding its potential for reuse in restoration projects for the houses of the Kasbah of Algiers.

The test results presenteddata extracted from these samples, having dimensional and discussed in this article compositional characteristics different from those required by current standards, represent the reference for structural analyses of the houses [7] and enrich the database onrelating to the physical and mechanical and physical properties of the historic building materials from the Ottoman era. It is relevant to present these different tests and results in a single paper in order to carry out a global rather than local analysis of the building materials used and the construction system.

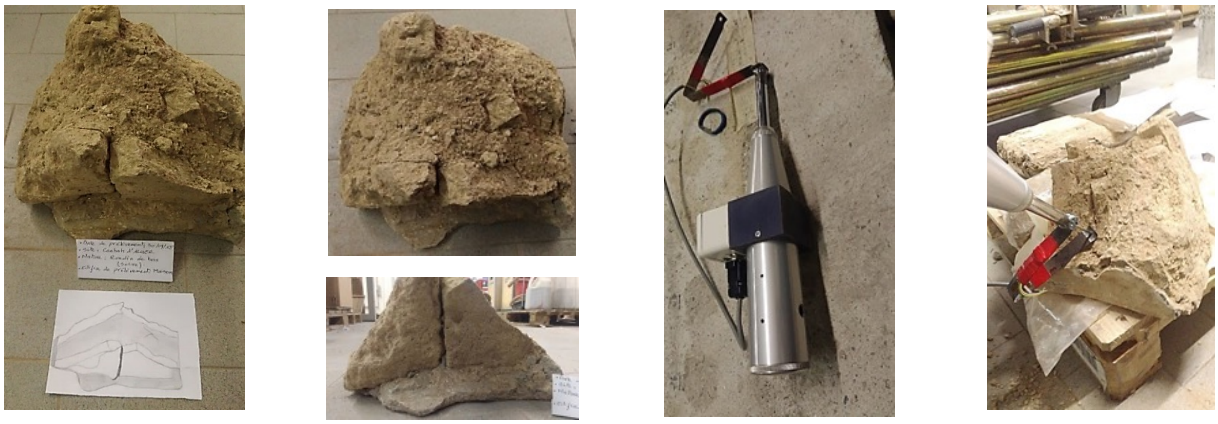

Figure 1 a) and b) Fragment of wall extracted in situ, c) Penetrometer, d) application of the Penetrometer (Source: author).

Figure 2. a) and b) Resistograph application c) partial result (Source: author).

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A New Multi–Method Approach for the Characterization of Structural Mortars from Roman Urban Sites in Central Italy

1. Introduction

This paper presents the preliminary results of a collaborative research project led by a team of archaeologist from the University of Missouri centered on the archaeometric investigation of Roman concrete construction at the sites of Pompeii (Campania) and Gabii and Pompeii, as part of a broader campaign of excavation and study of pluri-stratified monumental foci (the so-called "Area Urbana" complex and the Sanctuary of Venus, respectively(Latium). A range of analytical techniques is being employed to determine the composition, texture, and mineralogy of structural mortars sampled from stratigraphically dated architectural features. that are being documented through survey and excavation at pluri-stratified urban foci, the so-called "Area Urbana" complex and the Sanctuary of Venus, respectively. We discuss how Neutron Activation Analysis (NAA) can be applied in combination with Raman Spectroscopy to identify technological choices and elucidate their evolution over time (from the 2nd century BCE to the 3rd century CE) and space (the Alban Hills and Somma-Vesuvius catchment areas). By processing the NAA mortar data with principal component analysis (PCA), and then further investigating groupings with Raman Spectroscopy, we were able to reveal previously unknown trends in the mortar composition. The results also demonstrateaim to reveal the extent to which recipes and fabrication methods correlate with structural function. Our presentation will focus on the preliminary results from the NAA and PCA analysis and how such a combination of archaeometric techniques and statistics can be applied in Roman mortar studies.

2. The Case Studies: Periodization and Building Techniques

2.1. The Sanctuary of Venus at Pompeii

The Sanctuary of Venus in Pompeii is a monumental complex whose architectural development dates between the late 1st century BCE and the mid-1st century CE (Mogetta et al. 2022). The original site features a temple podium surrounded by porticoes on top of an artificial terrace supported by vaulted substructures. These structures were built using variants of volcanic ash-hydrated lime mortar mixed with stone rubble of different origins and grade, such as local concretionary limestone (known as "Calcare del Sarno"), compact lava, lightweight scoriae, and volcanic tuffs predominantly quarried from alkaline and highly alkaline deposits of Somma-Vesuvius (Kastenmeier et al. 2010). Minor modifications are attested in the Claudian period, whereas a second major phase of development is represented by opus reticulatum structures featuring Neapolitan Yellow Tuff facing blocks. Below the temple construction fills, a 2nd-century BCE horizon has been uncovered, whose remains also include variants of mortared rubble architecture predominantly made with large Sarno Limestone elements. A total of 73 samples were collected from The compositional study of the binders aims to investigate how variation in building techniques correlates with the stratigraphic periodization, and whether specific recipes were judiciously selected depending on the structural purpose or load requirements of the architectural units.

2.2 The so-called "Area Urbana" site at Gabii

Gabii is a top-tier urban center located 12 miles east of Rome whose occupation spanned from the 9th century BCE to the early Medieval period[1]. Recent excavations around the site's main intersection (Areas J, G, H of the Gabii Project) have revealed a cluster of public monuments built in ashlar masonry during the Mid-Republican period, all of which exploit local volcanic stones (the prized lapis Gabinus and variants of Anio Tuff). After a phase of abandonment in the Late Republican period, the site was extensively redeveloped to incorporate commercial infrastructure and other utilitarian buildings. Two main building phases are attested: an opus reticulatum phase dating to the mid-/late 1st century CE and opus vittatum phase dating to the late 2nd and 3rd century CE. In both periods, concrete construction relied for large part on the recycling of blocks and other demolition materials taken from the Mid-Republican monuments. The dataset from Gabii, consisting of 82 samples, enables us to evaluate compositional variation across different geologic regions (Latial v. Campanian volcanism[2]), as well as to characterize the evolution of techniques through periods not represented in Pompeii.

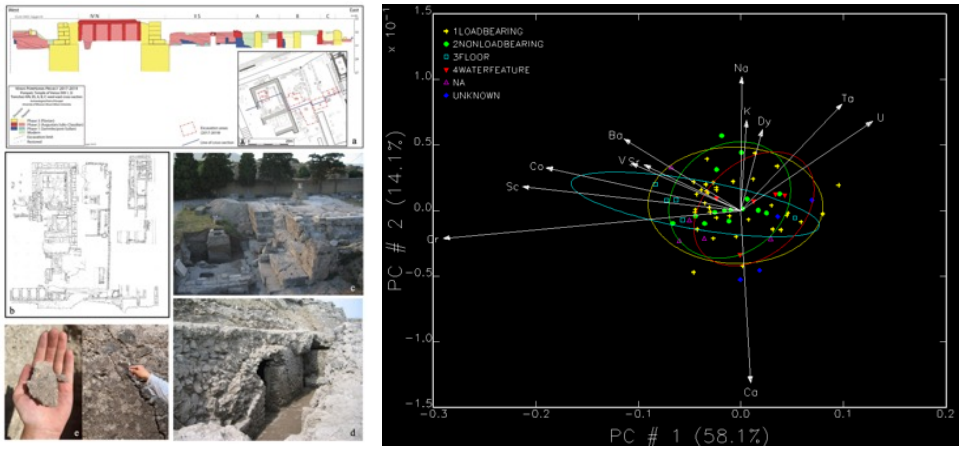

Figure 1. Left: Cross-section (a) and plan (b) of the Sanctuary of Venus excavations in Pompeii. Detail views: (c) concrete grid of the temple podium and foundations of its exterior ashlar façade; (d) vaulted substructures supporting the terrace in front of the temple, from which the sample shown in (e) was taken. Right Biplot of PCA #1 and #2 of the Sanctuary of Venus's mortar samples based on elemental composition from NAA data. The vectors indicate which elements are driving the most variation in the mortar.

3. Analytical Methods and Preliminary Results

All samples collected from the sites under investigation were analysed with NAA in accordance with the standard procedures at the Archaeometry Laboratory at the University of Missouri Research Reactor (MURR). The quantitative elemental data resulting from NAA was then analysed using multivariate statistical techniques–primarily Principal Component Analysis (PCA) and Cluster Analysis[3]. This application of multivariate statistics to bulk elemental data from mortar is not dissimilar to the methodology used in Dilaria et al.'s study of the Sarno Baths at Pompeii[4]. In Figure 1, grouping the samples by function at the Sanctuary of Venus revealed correlations between the mortars' structural function and recipe. The load bearing mortars (yellow) had the most amount of variation in both PC #1 and PC #2. Floor mortars (blue) had more variation in PC #1 but very little variation in PC #2. In considering the elements driving variation in PC #2, the floor mortars sampled from the Sanctuary of Venus at Pompeii had relatively consistent

1 Samuels et al. 2021.
2 Marra et al. 2011.
3 Glascock and MacDonald 2023.
4 Dilaria et al. 2021.

amounts of calcium in the recipes compared to the other groups examined. The variation in the composition of the non–load bearing mortars (green) is evidently driven by a number of elements, whereas that of the water features on site is largely driven by calcium, tantalum, and uranium. The patterns revealed in the PCA enabled us to select samples representative of groups for further analysis–for the purpose of this presentation, this largely involved Raman spectroscopy.

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Evaluation of the fire passive protection degree of a 19th century mortar applied on the vaults of the Saint Lazare cathedral of Autun

1. Project presentation

The construction of Saint Lazare Cathedral, Autun began around 1120 through the initiative of Etienne Baugé and has been completed in 1146. The vaults partially restored in the 19th century by Eugène Viollet-le-Duc to stabilize the monument, are made up of a broken vessel and punctuated by equally broken transoms with double rollers. The nave is made up of seven bays, six of which have been reconstructed as a light vault made up of an assembly of hollow terracotta bodies leveled on the extrados by a 70 mm thick shaped mortar, Figure 1a. As part of the improvement of fire protection, a study was carried out to characterize the ability of the mortar to passively protect the sensitive hollow elements and then, if needed, to develop a fire protection strategy. Due to its strong heritage character and its geometry, it was not possible to collect sufficient samples for an exhaustive characterization of the Thermo, Hygro, Chemo, Mechanical (THCM) behaviour. It was therefore decided to carry out an exhaustive physico-chemical characterization of this mortar from a collected macro-sample and to clone it to obtain a sample large enough to carry out fire tests at macro scale, Figure 1b-d. Used samples are squared (55x55 cm^2) with constant thickness to simulate a part of a structure. Each of them has been heated by fixing the standard fire ISO834 on one face.

2. Physico-chemical analyses and replica development

The combination of thermal and mineralogical analyses helps us to demonstrate that mortar is made with hydraulic lime but it's also distinguished by its granular skeleton, Figure 1c; in fact, the latter is mainly made up of tile fragments giving it a pink-orange hue. It has a relatively developed porosity of almost 38%. Its thermal signature highlights only few phase transitions with mainly an endothermic phenomenon between 60°C and 165°C corresponding to dehydration involving the evaporation of free water and structural water of the CSH. This structural water comes from the hydraulic setting of the lime, generating the following reaction:

2 (2CaOSiO2) + 4H2O → (3CaO2SiO23H2O) + Ca(OH)2

Then an endothermic phenomenon between 360°C and 418°C corresponding to a dehydroxylation of a clay phase and probably resulting from imperfect cooking of the tile used as a granular skeleton. Finally, an endothermic phenomenon between 767°C and 829°C corresponding to the decarbonation of lime has been identified. This is the process of thermo-chemical decomposition of calcite with a release of carbon dioxide corresponding to the initial quantity for its formation according to the following reaction:

Ca(OH)2 + CO2 → CaCO3 + H2O → CaO + CO2

The identification of the main chemical phases and their thermochemical decomposition, the estimation of the granulometry tendency and the evaluation of proportion of the constitutive materials by optical analyses and the determination of the insoluble residue allows an approach of the original composition of the mortar. Finally, a formulation has been proposed and adjusted to obtain a material density close to 1650 kg.m-3. The comparison of the thermochemical behavior for both the original and the clone is quite similar.

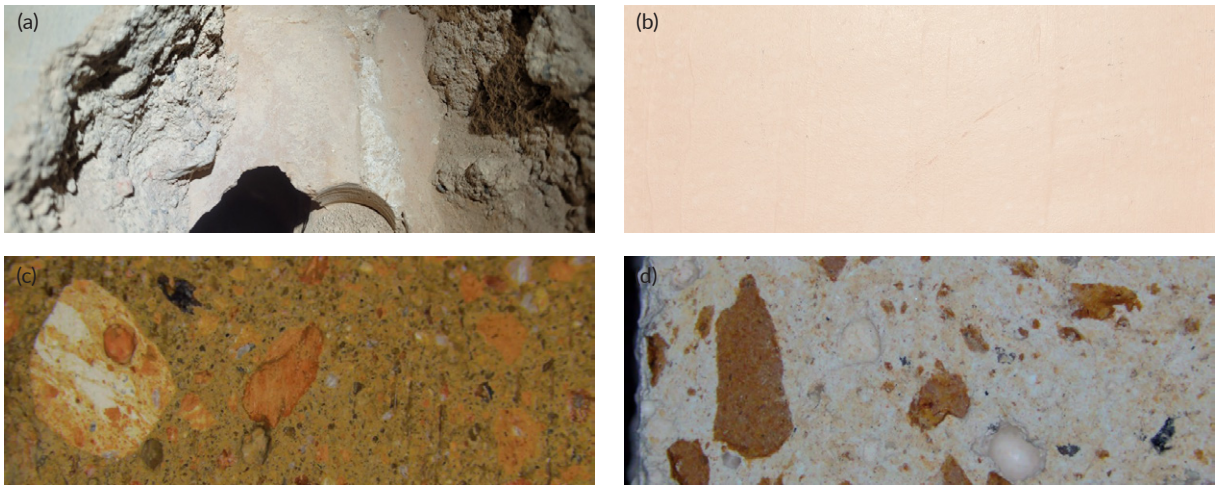

Figure 1. (a): original 19th century mortar shaped on vaults and (c) microscopic view – (b): macro and (d) micro-view of the cloned mortar.

3. Fire resistance testing

3.1 Sample instrumentation and experimental protocol

For the study, the behavior of a square plane sample (0.55 x 0.55 m²) with constant thickness (40 mm) subjected to a calibrated temperature rise is sought. The sample is used to close a horizontal radiant furnace and the standard ISO834 is fixed on the down face in order to simulate a test configuration with high thermal gradients from the exposed side to non-exposed side of the plate. In the central part of the sample, an array of sheathed type K thermocouples is made between the exposed face and the unexposed face, Figure 2a. In addition to this instrumentation, an infrared thermal camera (FLIR T650sc) is used to record the radiative thermal flux emitted naturally by the sample on the unexposed side and stimulated by heating. An illustration of the 2D radiative flux distribution on the non exposed side is given in the Figure 2b. The sample mass is also registered before the fire test and just after a fixed heating time.

3.2 Samples behaviour during the fire test

The sample is simply placed on the furnace and a mineral wool gasket ensures the thermal sealing. The sample is therefore relatively free to deform on the furnace-sample contact areas. Then, the exposed

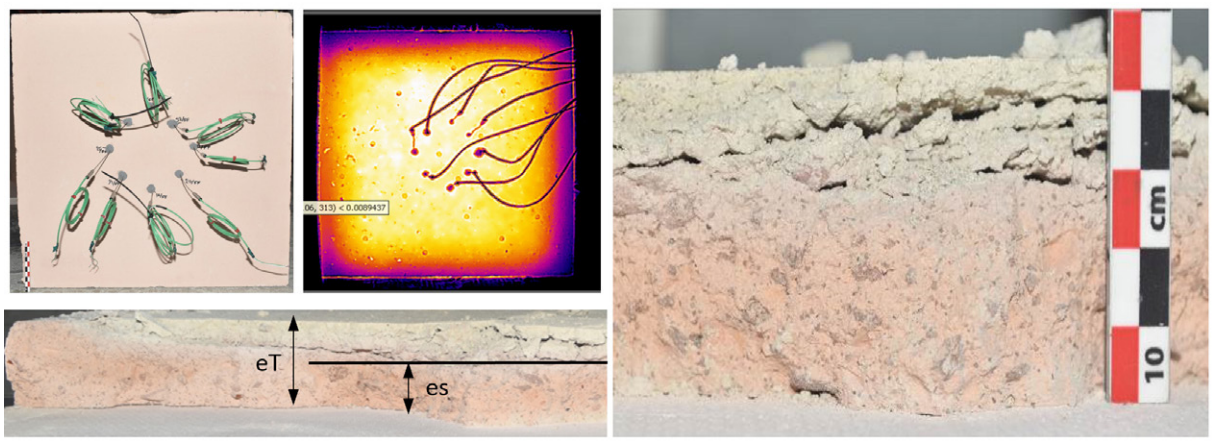

Figure 2. (a): plate before testing –(b): infrared imaging after 3 hours 45 minutes of testing – (c, d): plate after testing (eT = total thickness; es = thickness poorly affected by decarbonation) after 3 hours 45 minutes of testing.

side is represented by the molded face of the sample. Such a procedure helps us to control the surface roughness exposed to equivalent fire. The surface of the unexposed side is smoothed manually with a ruler. During the test, no mechanical damage has been observed at the non-exposed side. 3D scanning of the unexposed side before the test, after 45 min and after 3h45min testing (maximum duration testing) shows that the sample collapses with a maximum recorded at the center of the slab (~1.5 mm). Logically, heat exposition modifies the mechanical properties of the material which exhibits dilatant behavior during the temperature rise. Such an observation is explained by the dominance of lime in the formulation. At the end of the test, the slab weighing shows a slight mass loss ($\Delta M/M_0 = 5.1\%$) which can be explained by a process of dehydration and partial decarbonation of the material. After cooling, the damaged state of the sample is distinguished by a structural stratification parallel to the exposed and non exposed side., Figure 2c-d. This observation suggests a 1D damage pattern (expected) between the exposed face and the unexposed face and induced by the used device. This damaged state is illustrated in Figure 2(c, d) and showsImage analyses from exposed side to non exposed side allow that during the test 30% of the thickness has been probably chemically damaged.

3.3 Thermal transfer results

During the fire test, the obtained thermal transfer induced by the fixed thermal loading is highlighted, Figure 3. The temperatures registered near the exposed side are very consistent with the standard ISO834. Those results show for each position along the thickness signals in good consistency with the fixed temperature at the exposed side except a detected plateau when the local temperature reaches 90°C. Such a plateau highlights the effect of dehydration and then dehydroxylation process previously suggested in the parts 2. and 3.2. The effect of dehydration of the board is clearly detected by the short thermal barrier which induces the temperature blockage during the transport of the dehydration front. After this period and because of the highlighted thermal transfer, an insulation behaviour seems dominate the thermal properties of the material and its structure. Such qualification is deduced from the thermal gradient analysis, Figure 3. The identification of the thermal transfer through several thermocouples localised from the exposed side to non exposed side allow a good approximation of the temperature reached at different altitudes from the non exposed face during the test by interpolation. The results also allow the temperature signals to be reconstructed at the unexposed face (z = 0 mm) and at the exposed face (z = 40 mm) by extrapolation. Since the sensors are placed at the center of the slab, they report the thermal state while freeing themselves from edge effects. Finally, the registration of the radiative thermal flux at the non exposed side exhibits a representative average flux (low surface thermal heterogeneities) over the entire surface of the sample.

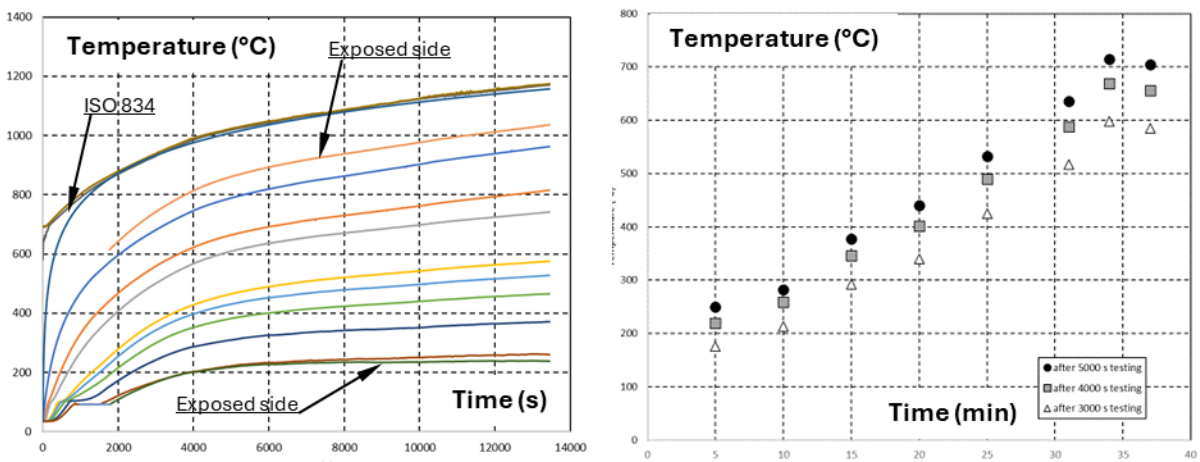

Figure 3. Illustration of the obtained thermal transfer through the studied mortar and illustration of the thermal gradient after fixed duration during the fire test.

4. Conclusion

The reconstitution of the original mortar formulation applied on the vaults of the St Lazare Cathedrale as been proposed by mimetism. Such methodology helped us to study the behavior of the historical mortar under fire condition. The casted samples have been tested horizontally through ISO 834 fixed on the underside. Obtained results show a good mechanical stability of the mortar during 3h45. Analysis of the propagation of the maximum $\Delta T = 180°C$ reached to the non exposed side of the board highlight a fire resistance close to 4000s. Eventhough the mortar has been probably not developed initially to passively protect the vault, the TCM consideration exhibit a relative good behavior in fire condition. Dehydration and dehydroxylation processes and a partial decarbonation characterize the thermochemical damages of the mortar. Finally, those results will be then use to study the better strategy to reinforce the passive protection of the vaults.

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Topic 2

Historic production, processing and application of mortars, renders and grouts. Lime technologies

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Provenance of the raw materials used in the mortars of Hagia Sophia (Istanbul, Türkiye)

The aim of this study is to hypothesize the provenance of the raw materials used to produce the ancient mortars of the structure of Hagia Sophia (Istanbul, Türkiye) through archaeometric analysis. Several studies had previously been conducted to determine the compositional characteristics of Hagia Sophia's mortars[1-2]; however, the sources of the raw materials used in the building materials of Hagia Sophia have never been investigated.

For this study, 26 new samples of mortars were taken from the building, that belong to the construction and restoration stages of Hagia Sophia between the 5 th and 15 th centuries.

Moreover, a total of 133 geological samples, were taken from different geological formations in Istanbul and its surroundings, according to the rock types identified in the mortars and the lime production places mentioned in Byzantine and Ottoman written sources.

All the samples were analyzed by Optical Microscopy on Thin Sections, X-Ray Fluorescence Spectroscopy (XRF), X-Ray Powder Diffraction (XRPD) and Micro-Raman Spectroscopy (MRS). The petrographic analyses performed on thin sections of the mortars and geological samples using optical microscopy with transmitted polarized light played a crucial role in achieving the objectives of this study.

The identification of rock fragments in the mortar aggregates, such as granite, arkosic sandstone, quartzite-quartzarenite, graphite needles fragments, and limestone rock fragments, highlighted that the mortars are compatible with the geological formations of the Anatolian side of Istanbul. In particular, granites can be associated with the Sancaktepe Formation; arkosic sandstone can be associated with the Kurtköy Formation; quartzite-quartzarenite with the Ayados Formation, and graphite and limestone with the Pelitli Formation within the region. These formations are found exclusively on the Anatolian side. The distance between these formations and Hagia Sophia ranges between 10 and 35 km. This means that, for many years, the aggregates used to prepare the mortars of Hagia Sophia were sourced just a few kilometers from it.

The results included at the end of the study will constitute an important database for subsequent restoration works at Hagia Sofia, as it is important to determine the provenance of the original raw materials to obtain new compatible building materials for its conservation.

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On waterproofing recipes in Nea Paphos, Cyprus – a world of open questions

1. Introduction

This paper aims at offering an interpretation of the hydraulicity degree in a set of historic mortars collected from the site of Nea Paphos (Cyprus) and analysed through an interdisciplinary approach. Eventually, determining the hydraulic character of a historic mortar is a matter of careful evaluation of multiscale data, starting with the interpretation of the context and ending with the characterization of the mixture components.

The samples collected from the site all pertained to water and liquid-related structures related with the storage and disposal of water or other types of liquids. After the analytical procedure, it was possible to categorize and define the physical and chemical properties of the samples in relation to their water containment function. At least two different types of renders for water-related structures were used in Paphos between the Late Hellenistic and the Roman periods: one group was composed of air lime binder with pozzolanic aggregates, while the second was a mixture of lime with natural hydraulic lime-based mixtureproperties enriched with pozzolans.

2. Methodology

In order to assess the hydraulicity of the samples, it was necessary to thoroughly characterize the binder and aggregates' composition following the analytical procedures already commonly in use in the field of mortar studies[1]. Preliminary macroscopic evaluations were followed by the preparation of blue-stained, polished thin sections, which were analysed under a standard petrographic microscope. To acquire mineralogical data, a small fraction of the samples was ground to analytical fineness and analysed in XRD-QPA following the Rietveld method. TA-DSC and EGA have been employed in this study in order to obtain quantified chemical composition data[2].

Furthermore, TA measurements provide an estimate of possible hydraulicity via the calculation of the ratio[3] between the loss of H2O in the 200°–600°C region and that of CO2 in the 600°–900°C one. This ratio allows to categorize lime binders in pozzolanic (ratio < 3), hydraulic (ratio 3–9), and aerial (ratio > 10). Hydraulicity was also assessed via the estimation of the cementation index (CI) of the binder. The data for the calculation of the CI were collected by using SEM-EDS point analysis. Our set of analyses was completed by water absorption an open porosity testing.

3. Results and conclusions

This brief study allowed us to compare some suitable techniques for the evaluation of the hydraulicity degree of historic mortars. Hydraulicity is a complex property to estimate, and a single analytical technique

1 Alvarez et al. 2021; Kozlovcev, Válek 2021; Singh, Waghmare, Vinodh Kumar 2014; Letourneux, Feneuille 2012; Groot et al. 2004.
2 Cavalheiro 2019.
3 Moropoulou, Bakolas, Bisbikou 2000.

is not sufficient to safely demonstrate the presence and the extent of such property. The calculation of the H2O/CO2 is definitely a rapid and efficient way to test hydraulicity; however, this technique alone does not allow to evaluate whether the hydraulic character is conferred by silica-aluminates contaminants in the raw material or by addition of pozzolans. Likewise, calculating the CI alone – whether from XRF or SEM-EDS elemental composition – does not grant a correct evaluation of the samples. As demonstrated in this study, CI values can easily be increased by the presence of silica and alumina which are not reactive and not participating in any hydraulic reaction. High CI values do not necessarily reflect high hydraulic properties. A careful evaluation of the thin section under petrographic and scanning-electron microscopes allow to more consistently and accurately identify the presence of particles suitable for the production of hydraulic phases. This paper highlights another issue occurring in the analysis of lime-pozzolan systems in particular: the presence of reaction rims. While often reaction rims are associated with a hydraulic nature of the sample, it must be pointed out how they can be only physical reactions and not chemical. In fact, apparent reaction rims can be caused by a denser layer of binder, which accumulates on the edges of the ceramic particles due to their increased porosity, and hence higher absorption property. Effectively, this phenomenon creates rings around the ceramic particles that might be wrongly interpreted as reaction rims. Although CSH or CASH phases were not observed in XRD-QPA, among the analysed samples a relative high amount presents hydraulic properties to some extent, with eight samples possibly corresponding to NHL binders enriched with pozzolans, a technique already observed in other studies[4]. Only two samples among the lime-pozzolans systems present hydraulic properties, indicating the preference of the local craftsmanship towards NHL rather than lime. This observation in particular is in contradiction with what is widely accepted among scholars and professionals investigating Roman plasters; in fact, several sources, both historic[5] and modern studies[6], indicate a predominance of air lime mixed with pozzolans – natural or artificial – rather than NHL plasters in Roman masonry. It must be also noted that the lime-pozzolan system, widely associated and attributed to Roman technologies[7], was used in Cyprus as early as the Late Bronze Age. In conclusion, this study highlights how difficult it is to properly categorise archaeological plasters as NHL or hydraulic. The adoption of numerous different terminologies – often misused – further conditions this complicated assessment. This talk offers some perspective on the methods to cautiously evaluate the hydraulic properties of a samples and clarifies on terminological issues that often plague the field of archaeological sciences.

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Cocciopesto lime plaster: a traditional composition from ancient times to the present day

1. Introduction

Plasters, made by mixing lime with dust and fragments of bricks, tiles or pottery, have been the essential material of ancient aqueducts, bridges, and baths due to their durability. They are often called cocciopesto from the Renaissance until today, and the Romans called them opus signinum[1]. Their use can be considered as an ancient tradition. It dates to the time of the Kingdom of Solomon (970-931 BC). In the Greek period they were used as wall plaster, flooring and as mortar in arches, foundations, and cisterns. In Roman times, they were generally used on walls exposed to water in baths, cisterns, aqueducts, and bridges. They were also used as insulation on floors and pavements and as a support for mosaics2. Their use in the wet and humid areas of buildings was widespread in the Mediterranean region from the Roman, Byzantine and Ottoman periods until the nineteenth century. In this study, the properties of cocciopesto mortars and plasters from some buildings of the Roman, Byzantine, pre-Ottoman and Ottoman periods in Anatolia were investigated. The aim was to determine their basic physical and mechanical properties, raw material composition, microstructural and hydraulic properties, mineralogical and chemical composition of their lime binder and fine aggregates, to establish common features for use in the Roman, Byzantine and Ottoman periods in Anatolia.

2. Materials and method

In this study, 17 plaster samples were collected from Ottoman and pre-Ottoman baths, Byzantine churches and Roman stadiums, baths and bouleuterions in Western Anatolia. The ancient baths of Aydın and Selçuk have been selected from the Ottoman and pre-Ottoman period examples. The church of Anaia (Kadıkalesi) and the church of St. Jean (Ayasuluk) were selected from the Byzantine examples in Western Anatolia. The Gymnasion at the ancient site of Aigai (Manisa) was chosen as a Roman period example to study the characteristics of cocciopesto plasters.

Multi-analytical analyses were carried out on the plaster samples to determine their basic physical properties, raw material compositions, chemical and mineralogical composition, microstructural properties and hydraulic properties. Bulk density and porosity were determined using standard test methods. The amount of lime and cocciopesto aggregates was determined by dissolving carbonated lime in dilute hydrochloric acid. The mineralogical compositions of the fine plaster matrices and cocciopesto aggregates were determined by XRD analysis. Their chemical compositions and microstructural characteristics were determined using SEM-EDS. Pozzolanic properties of the cocciopesto aggregates were determined by measuring the differences in electrical conductivity (mS/cm) before and after the addition of the fine aggregates (<53 μm) to saturated Ca(OH)2 solution using a conductivity meter. Hydraulic properties of plasters were evaluated by TGA analysis, defining the weight loss between 200-600°C and 600-900°C.

1 Artioli, Secco, Addis 2019.

3. Results and discussion

Cocciopesto plasters were pink in colour and low dense and high porous materials. Their lime binder and aggregate ratios were between 0.3-2.0 by weight, and aggregates greater than 500 microns were the largest fraction of the aggregates. The strong adhesion of aggregates to the lime binder indicates thorough mixing of cocciopesto aggregates with lime in plaster production. Cocciopesto aggregates consisted mainly of quartz (SiO2), albite (Na(AlSi3O8)), illite-like phase and haematite (Fe2O3). The presence of illite phase and the absence of the high temperature products such as mullite in all cocciopesto aggregates showed that their firing temperatures were below 900°C. When clay minerals are fired below 800 °C, a significant amount of silica remains as an amorphous phase[2]. Such amorphous phase is highly reactive and can give rise to hydraulic compounds when reacted with lime. Aggregates were composed of high amounts of silicon and aluminium, moderate amounts of iron, magnesium and smaller amounts of sodium, potassium, and titanium (Table 1). All cocciopesto aggregates had significant pozzolanicity. The hydraulic properties of the plasters were determined by TGA analysis by calculating the ratio of the weight loss due to the release of chemically bound water (BW) from hydraulic compounds between 200-600 °C and the weight loss between 600-900 °C due to CO2 gas from the decomposition of CaCO3 of the plasters. The CO2/BW ratios of the cocciopesto plasters were less than 10, ranging from 1.2 to 8.0. Therefore, all the samples of cocciopesto plasters could be considered hydraulic due to the use of pozzolanic cocciopesto aggregates. SEM analysis showed that the cocciopesto aggregates were well adhered to the lime binder suggesting that the plasters were made by a process of thorough mixing of the cocciopesto aggregates with the lime. Brick-lime interface consisted largely of calcium, silicon and aluminium that may indicate the formation of hydraulic compounds such as calcium silicate hydrates and calcium aluminate hydrates. Plasters have self-healing properties due to the dissolution, transport, and re-precipitation of carbonated lime binder in the fissures and microcracks of the plasters and the pores of the cocciopesto aggregates (Figure 1). The self-healing properties make them durable and stable by the precipitation of calcite crystals in voids or along cracks in the plaster.

Site	Sample Name	Mineralogical Compositions	Chemical Compositions of the aggregates (%)								Pozzolanic Activity
			SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	(mS/cm)
AIGAI GYMNASION	AI1	Qtz, Ab, An	70,4	13,4	5,4	2,1	3,3	0,7	0,9	1,0	6,7
	AI2	Qtz, Ab, An	60,9	15,2	5,5	2,6	2,6	2,2	1,4	1,0	3,5
AYASULUK ST. JEAN CHURCH	AS1	Qtz, Ilt, Ab, Hem	59,2	17,1	9,9	8,0	1,5	0,7	2,8	0,7	5,8
	AS2	Qtz, Ilt, Ab, Hem	69,2	12,9	7,3	4,8	1,7	0,5	2,0	1,5	7,7
	AS3	Qtz, Ilt, Ab, Hem	81,6	6,8	5,5	3,7	0,7	0,2	0,9	0,6	7,7
KADIKALESİ ANAIA CHURCH	KA1	Qtz, Ilt, Ab, Hem	73,4	13,6	6,1	1,4	0,8	1,0	2,9	0,8	7,6
	KA2	Qtz, Ilt, Ab, Hem	67,2	16,8	7,3	2,1	1,2	1,0	3,8	0,7	5,7
	KA3	Qtz, Ilt, Ab, Hem	66,1	14,4	7,8	3,0	4,1	0,5	3,0	1,0	7,9
AYDIN BATHS	A1	Qtz, Ilt, Ab, Hem	63,5	19,4	8,1	2,6	1,5	-	3,9	1,0	7,6
	A2	Qtz, Ilt, Ab, Hem	81,5	10,2	3,8	1,5	1,2	-	1,7	0,8	6,6
	A3	Qtz, Ilt, Ab, Hem	68,6	16,2	7,3	2,8	1,3	-	3,1	0,8	7,8
	A4	Qtz, Ilt, Ab, Hem	69,8	15,0	4,4	2,4	1,0	-	3,1	1,0	8,0
	A5	Qtz, Ilt, Ab, Hem	83,9	8,2	4,2	0,4	0,3	-	1,1	0,7	7,6
SELÇUK BATHS	I1	Qtz, Ilt, Ab, Hem, Dol	69,7	14,1	7,8	4,1	1,0	0,4	2,1	0,9	7,0
	K1	Qtz, Ilt, Ab	61	17,7	9,5	5,9	2,0	0,6	2,3	1,0	6,0
	Y1	Qtz, Ilt, Ab, Hem, Dol	69,7	14,1	7,1	4,8	1,0	0,9	1,6	0,8	6,5

Table 1. Mineralogical and elemental composition and the pozzolonicity of the cocciopesto aggregates. (Ab: Albite, An: Anorthite, Dol: Dolomite, Hem: Hematite, Ilt: Illite, Qtz: Quartz).

2 Cultrone, Carrillo-Rosua 2020.

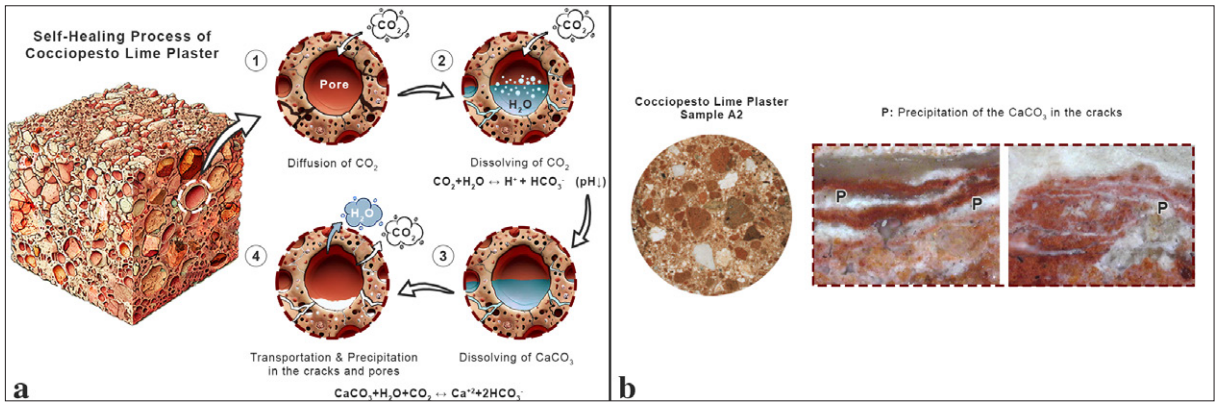

Figure 1. (a) Schematic representation of the self-healing process of the cocciopesto lime plaster b) Optical microscopy images of cocciopesto plaster.

4. Conclusions

The cocciopesto plasters that were used in different periods of time have almost the same physical, mineralogical, and chemical characteristics. Their lime/aggregate ratio varies from 0.2 to 2.5 by weight. Cocciopesto aggregates were fired at temperatures below 900 °C and have pozzolanic properties. Plasters are hydraulic due to the mixing of pozzolanic cocciopesto aggregates with lime. They have self-healing properties that make them durable and stable in wet and humid conditions of structures without the need for renewal. All these characteristics can be a common reason for their use as plasters in wet and humid areas of structures from ancient times to the present day.

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Preliminary study of the gilded stucco decorations in the St Peter Basilica in Rome

1. Introduction

The planned restoration works of the mid-16th c. and 18th c. gilded stuccoes of the vault of the St Peter Pope Basilica in Rome were anticipated by a detailed pilot study of the duration of a few months to plan an adequate conservation strategy. The selected area of this preliminary work was on a limited sector of the north transect of the vault (Figure 1A). During this time, a first sampling was conducted with the scope to gather information concerning the materials and techniques used for the preparation of the individual layers of the stratigraphic sequence (Figure 1B). In this paper, the focus is on the analysis of the ground and finishing layers of the stucco decoration.

The first stuccoes were executed in the mid-16th c. when Michelangelo Buonarroti was architect responsible of the works for the construction of the Basilica. In the first half of the 17th c., the stuccoes were executed on the vault of the nave under the direction of the architect Carlo Maderno. The ornamentations were concluded in the middle of the 18th c. Documented restoration works occurred at the end of the 19th c.

2. Materials

The restricted area of the pilot study (and the consequent impossibility to reach the entire decoration) limited the sampling strategy and allowed for a preliminary selection based on stylistic features, decay

Figure 1a.

Figure 1b.

Figure 1. ENS18 painting of the Harpist House on the left (R. Benali, Inrap – MDAA), and microphotographs of the sample in thin section (in plane polarized light on the left side and crossed polarized light on the right). The angular grains visible in A and B are calcite crystals rich in macles. In C the limit between the finishing layer (in the upper half of the image) and the preparation layer, a lime mortar with quartz sand (A. Coutelas).

patterns, spontaneous samples. Six samples (Table 1) were collected (also including those for the analysis of the gilding technique not discussed here).
Petrographic analysis was carried out using a polarizing light microscope (PLM) Zeiss Axioskop 5 equipped with a digital camera Axiocam for capturing images with resolution 5.0 Megapixel. Point counting was operated on at least 600 points for each examined thin section. In addition, complementary studies were carried out for the determination of the microstructural features and microchemical analysis using an electron microscope coupled with an energy dispersive X-ray spectrometer (SEM/EDX). A Phenom desk electron microscope (Thermo Fisher Scientific Ltd) was used with the following setup: 15KV, LV, wd 7.8 mm, BSE detector. Finally, X-ray powder diffraction (XRPD) was carried out for qualitative mineralogical phase determination using QualX2.0 (Altomare et al., 2015). A Rigaku Miniflex 300 was used operating in Θ-2 Θ mode, 30KV, 10mA, Cu anode (Cu Kα=1.5418 Å), 2-Theta range 5-55 degrees, increment 0.02°, scan speed 0.5°/min, no spin.

ID	Sampling area	Description of the layers
SV_SP_trN_NO_01	Northern transect, alternated astragalus and small beads	Complete stratigraphic sequence of a small bead
SV_SP_trN_NO_02	Northern transect, frame composed of festoons	Finishing mortar of a leaf
SV_SP_trN_NO_03	Northern transect, frame composed of festoons	Ground and finishing layer of a fruit
SV_SP_trN_NO_04	Northern transect, frame composed of festoons	Ground layer of a fruit
SV_SP_trN_NO_05	Northern transect, frame composed of festoons	Finishing layer of a fruit
SV_SP_trN_NO_06	Northern transect, frame composed of festoons	Finishing layer and gilding of a fruit

Table 1. Description of the samples analysed during the pilot study.

3. Results and discussion

The petrographic examination of the ground layer indicates that the mortars were formulated with air lime composed of calcite and the addition of (mainly) poorly sorted red pozzolans with grain size ranging from coarse to medium-fine and very fine sands. Rare pozzolanelle and individual crystals of clinopyroxene (diopside) and leucite were detected. The presence of analcime, hematite, biotite completes the mineralogy. The ratio binder vs aggregate is 1.5 by volume. The macroporosity is rather low ranging between 2-5% by volume. Red pozzolans exhibit the typical features of the intermediate alteration facies as leucite has fresh surface, is also replaced by analcime or dissolved (Jackson et al., 2007). Within the vesicles a thin film composed of Al and Si (Si/Al apx. 1) suggests the presence of clay minerals (halloysite?) responsible for the hydraulic reaction. The red pozzolan tephra correspond to those used by the Roman builders in the Imperial age and coming from the deposits erupted from Alban Hills volcano (Seymour et al., 2021; Marra et al., 2016; Jackson et al., 2011).
The finishing layer of variable thickness (depending on the features of the decoration motifs) is composed of air lime and crushed marble (marmorino). The maximum grain size MGS = 0.5 mm suggests that Carrara marble was used. The presence of quartz, phyllosilicates and dolomite is rare as well as the unintentional presence of red pozzolans. The proportion of the mix depends on the necessity of workability; the artists used more binder with respect to the calcite aggregate for the execution of leaves and less for the festoons.
The gold foil was applied with the missione technique using siccative oil mixed with Pb-based pigments (analysis and data not reported here).

4. Concluding remarks

The proposed research represents a first study of the technology of production of the decorative apparatus of the gilded stuccoes in St Peter Basilica in Rome that will be integrated and extended during the conservation works.

The petrographic and mineralogical examination of the ground mortars demonstrated that the artists knew very well the excellent technological properties of pozzolans (in particular, the red variety) extensively used by Romans during Imperial age. According to this evidence, they intentionally selected the same materials for the formulation of durable mortars used for the ground layer of the gilded stucco decoration.

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Effect of admixture in Traditional Korean Lime Technology

1. Background and Methods

1.1 Study background

Since 2020, NRICH has been conducting research on traditional Korean lime technology. In this process, we have focused on identifying the functions of traditional admixtures such as perilla oil, sticky rice paste and Hanji(traditional Korean paper), as described in old records like Uigwe;The Royal Protocols of the Joseon Dynasty. The purpose of this study was to verify the effects of perilla oil additive, which was a traditional admixture in lime mortar and to compare it with the effects of a waterproofing agent, a modern admixture with similar functions.

1.2 Sample preparation

The samples for the study were prepared using a high-quality quicklime powder available in the market and. The quicklime was slaked by the dry method. Equal amounts of water were used for slaking with the lime, and no extra sieving or curing processes were not performed. The ISO standard sand with a SiO2 content of over 98% and a moisture content of less than 0.2% was used as the aggregate. And the BinderThe binder(lime) and aggregate were mixed in a ratio of 1:2.(wt%). TheTwo types of admixtures were used in the sample were 2 types,, one traditional and one modern. First, the traditional admixture was obtained by cold-pressing perilla oil without heating. The proper amount and frequency of mixing and brushing were based on prior research conducted bywith old records. ThusAccordingly, 0.5wt% of perilla oil was mixed into the sample, and 5 timeslayers of perilla oil brushed. When perilla oil was were brushed on the sample surface, a. A hog bristle brush was used to brush the perilla oil on the sample surface, based on the information confirmed in the old records. InFor the case of modern admixture, a commercially available waterproof agent was used, and according to the usage instruction, water and the waterproofing agent were mixed in a ratio of 6:1 to be used as the mixing water of samples.

The lime mortar mixturemixtures were filled into 50×50×50mm cubed moldcube molds and dried inat a constant temperature and humidity (23°C, 50±3%), atand 5 days after filling the 5th day of filled into the moldmolds, the samples (dried mixture) were separated from the mold. And atmolds. On the 7th day, the samples were collected from the moldmolds and relocated into an acrylic holder to be cured under two conditions, curing and accelerated curing. The first condition curing, means curing in 0.04%

Sample Type	Binder	Aggregate	Mixing water		Admixture	
			Type	Ratio (wt%) (W/B+A)	Type	Amount
Blank	Powdered lime	ISO standard sand	Water	10	-	-
Perilla oil Mixed	Powdered lime	ISO standard sand	Water	9	Perilla oil	0.5wt%
Perilla oil Brushed	Powdered lime	ISO standard sand	Water	10	Perilla oil	5 times
Waterproof agent	Powdered lime	ISO standard sand	Water + waterproof agent	10	Waterproof agent	-

Table 1. Mixing proportion of samplessolvent, and (b) oil repellent (O) solvent.

concentration of CO2, and accelerated curing (AC) means curing in 5% of CO2 in a chamber. AC was conducted to investigate the long-term curing tendency of lime within a short test period.

1.3 Analysis methods

In this study, various spectroscopic analysis methods were utilized to identify the characteristics of the lime mortar. Samples were observed using a portable digital microscope (DG-3, Scalar, Japan) and measured with a spectrophotometer (CM-2600d, Konica Minolta, Japan). Waterproof characteristics were confirmed with a Contact Angle Goniometer (Phoenix 300 Touch, SEO, Korea) and customized freeze-thaw test equipment. Strength characteristics were identified with an ultrasound velocity measurement (Pundit lab, Proceq, Switzerland) and universal testing machine (AG-X plus, Shimadzu, Japan). Also, a carbonation test, X-ray diffraction analysis (X'Pert3 Powder, PANalytical, UK), Hyperspectral imaging analysis (FX10, FX17 and SWIR, SPECIM, Finland) with specialty software (ENVI, NV5, USA) and micro CT analysis (XT H 225, Nikon, Japan) with specialty software (VG studio, Volume Graphics, Germany) were performed to check the carbonation characteristics and determine the difference between the two types of admixture in the lime mortar.

2. Results

The blank samples and waterproof agent added samples were white, while the samples with perilla oil added was a light yellow color. Additionally, the surface of the perilla oil mixed sample was rough, which is assumed to be due to the difference in drying rates between the perilla oil and mixing water. On the other hand, no other color changes were observed due to the curing period. Notably, the traditional admixture with perilla oil showed excellent waterproof properties, and its effectiveness was improved when brushed. In contrast, the samples with modern admixtures did not show any significant difference in waterproof properties compared to the blank samples.

Lime is a building material used in masonry and plastering, so it is essential to verify its mechanical strength for on-site application. This study applied both destructive and non-destructive tests. In response to ultrasound velocity, the samples with traditional admixtures showed a slight superiority, while the significant compressive strength of samples brushed with perilla oil was observed. Although there were differences depending on the measurement method, it appears that the traditional admixture enhanced more. In the carbonation test, it was difficult to confirm the color boundaries of the samples with the traditional admixture, while the samples with modern admixture had relatively clear color boundaries,

Figure 1. Compressive strength by the admixture type.

making it easier to identify the carbonation area. In the X-ray diffraction analysis, the same minerals were detected in all three samples, and there were differences in diffraction intensity depending on the conditions of the additives. Differences according to the type of the admixture were also been confirmed in the micro CT and hyperspectral imaging analysis.

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Preliminary Findings on the Setting Process of Laboratory-Produced and Commercial Natural Hydraulic Limes

1. Introduction and methodology

Natural hydraulic limes (NHL, EN 459-1[1]) are hydraulic binders extensively used in restoration and sustainable construction, due to their chemical-physical compatibility with traditional materials[2]. They are mainly composed of lime (in the form of calcium hydroxide, called free lime), di-calcium silicate (C2S, belite) and tri-calcium aluminate (C3A, celite), even though low amounts of tri-calcium silicate (C3S, alite) and other aluminium and iron-bearing phases (e.g. C3A and C4AF) can also be found, depending on the initial composition of the raw material used and the manufacturing conditions[3]. Mortars made with NHL harden and set by two processes: 1) carbonation of calcium hydroxide in contact with atmospheric CO2; and 2) hydration of the hydraulic fraction when in contact with H2O. The latter process gives place to a series of hydrates (i.e. C-S-H, C-A-H and C-A-S-H) that are responsible for the higher mechanical strengths reached by NHL mortars compared to the aerial lime ones. However, NHL mortars may exhibit unexpected variability in their final mechanical strength because the hydration rate is strongly influenced by the water-to-binder ratio[4], and curing conditions and time[5]. This highlights the importance of monitoring NHL mortars or pastes throughout the early and mid-setting stages to accurately interpret the development of their final mechanical strength.

This study builds upon previous research on the production of natural hydraulic limes (NHL) using raw materials from southern Spain . Various NHLs with different degrees of hydraulicity (2, 3.5, and 5) were produced in the laboratory and mixed with water at a 1:2 w:b ratio to form NHL pastes. These pastes were maintained under high humidity (90 ± 5% RH) and CO_2-free conditions for the first 48 hours to promote the hydration of hydraulic phases. Subsequently, they were stored under lower humidity (70 ± 5% RH) and exposed to CO_2 to facilitate both hardening processes. X-ray diffraction (XRD) analysis was performed on freeze-dried NHL pastes at 2, 7, 15, 28, and 60 days, while a quantitative phase analysis using the Rietveld method was conducted before hydration and after 8 months. For comparison, commercial NHL pastes were prepared and analysed following the same procedure.

2. Results and discussion

The main differences in the mineralogy of the compared NHLs are related to the different raw materials used for their manufacturing (Table 1). It should be noted that only laboratory-produced NHL2 and NHL5 present hydrogarnet and AFm phases (CAĈH, monocarboaluminate, Table 1), generated from a partial undesired pre-hydration of C3A during laboratory slaking[6].

1 CEN 2015.
2 Groot et al. 2022.
3 Cowper 1927.
4 Xu, Wang, Sun 2015.
5 Álvarez et al. 2021.
6 Parra-Fernández et al. 2024.

Regarding the mineralogical changes taking place in all lime pastes during curing, a significant decrease in the intensity of the main portlandite XRD peak occurs at 28 days, but the carbonation is still uncompleted. In the laboratory-produced NHLs, a further transformation of hydrocalumite into monocarboaluminate is recorded after 2 days, displaying an initial high reactivity of the AFm phases towards both hydration and carbonation processes at early stages of setting. However, these phases do not evolve further during the study.

In general, the carbonation trend varies depending on the hydraulic degree of the studied NHL, justifying that limes might exhibit shorter or longer setting times depending on their index. Regarding hydration, the content of larnite (C2S), shows a decrease after 60 days in both commercial and laboratory-NHL2 pastes but instead remains stable in the most hydraulic limes at the same age. This can be explained considering the presence in NHL5 of higher contents of C3A and C4AF that are more reactive towards water than C2S.

At the end of the study (8 months later, Table 1), the carbonation process may be considered completed in all NHL pastes whilst the hydration process shows little differences depending on the type of lime. In general, a great reduction in the content of larnite is recorded, accompanied by an increase of the amorphous content, which can be explained by the transformation of C2S into non-crystalline C-S-H. However, this is more pronounced in the commercial limes than in the laboratory-made ones, since the former contains less Fe-bearing phases than the latter.

Sample	Per	Por	Cal	Arg	Qz	Crs	Lrn	Hrr	Bdi	Gh	C_3A	Bmlr	Hygr	CAĈH	Amor
NHL2 SA	-	42.64 (0.41)	24.35 (0.23)	-	2.64 (0.03)	0.84 (0.01)	13.50 (0.13)	1.55 (0.02)	-	-	1.73 (0.02)	-	-	-	12.80 (0.11)
NHL2 SA HY8m	-	0.01 (0.00)	58.24 (0.22)	6.22 (0.02)	1.68 (0.01)	0.74 (0.00)	0.11 (0.00)	0.27 (0.00)	-	-	0.35 (0.00)	-	-	-	32.38 (0.34)
NHL2	0.81 (0.00)	56.82 (0.30)	3.03 (0.02)	-	0.39 (0.00)	-	19.68 (0.10)	0.35 (0.00)	-	-	0.79 (0.00)	1.83 (0.01)	5.51 (0.03)	3.97 (0.02)	5.57 (0.63)
NHL2 HY8m	1.27 (0.01)	0.50 (0.00)	64.43 (0.32)	2.56 (0.01)	0.57 (0.00)	-	3.80 (0.02)	0.48 (0.00)	-	-	0.29 (0.00)	0.08 (0.00)	0.47 (0.00)	4.33 (0.02)	21.22 (0.52)
NHL5 SA	-	15.60 (0.10)	31.19 (0.21)	-	3.02 (0.02)	1.38 (0.01)	15.40 (0.10)	9.03 (0.06)	-	-	2.70 (0.02)	-	-	-	21.69 (0.68)
NHL5 SA HY8m	-	0.61 (0.00)	37.74 (0.17)	15.13 (0.07)	2.67 (0.01)	1.04 (0.01)	1.73 (0.01)	0.94 (0.00)	-	-	0.87 (0.00)	-	-	-	39.28 (0.39)
NHL5	1.40 (0.01)	18.51 (0.10)	1.29 (0.01)	-	0.02 (0.00)	-	40.19 (0.22)	0.18 (0.00)	3.75 (0.02)	1.80 (0.01)	0.08 (0.00)	2.98 (0.02)	10.30 (0.10)	4.64 (0.03)	13.96 (0.60)
NHL5 HY8m	1.12 (0.01)	1.11 (0.01)	14.86 (0.07)	25.00 (0.11)	0.77 (0.00)	-	10.13 (0.05)	0.60 (0.00)	2.17 (0.01)	2.18 (0.01)	0.10 (0.00)	0.10 (0.00)	5.22 (0.02)	-	36.63 (0.40)

Table 1. Mineralogical composition (standard deviations in brackets) of the studied limes. SA refers to Saint Astier NHL limes. HY8m: NHL pastes after 8 months of hydration. Per: Periclase, Por: Portlandite; Cal: Calcite, Arg: Aragonite, Qz: Quartz, Crs: Cristobalite, Lrn: Larnite, Hrr: Hatrurite, Bdi: Bredigite, Gh: Gehlenite, C3A: Tricalcium aluminate, Bmlr: brownmillerite, Hygr: Hydrogarnet, CAĈH: Monocarboaluminate.

Lime and wollastonite were detected in <1% in laboratory-manufactured NHLs.

3. Conclusions

This study underscores how different the setting of NHL can be, depending on the initial composition of the lime (which in turns depends on the raw material composition and the manufacturing conditions)

and its hydraulic degree, emphasizing the need for further research into the manufacturing of NHL to optimize its performances in construction and conservation applications.

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A review on maritime concrete in the Mediterranean area

Maritime concrete is vital for coastal and offshore infrastructure, especially in the Mediterranean, where ports and underwater structures have shaped economic and cultural development. The region's harsh marine environment—high salinity and chemical exposure—demands durable materials. As the Mediterranean region has a long history of maritime concrete use, it is of special interest to study this material emphasizing on Roman concrete, or opus caementicium, utilized pozzolanic materials such as volcanic ash from the Bay of Naples, which contributed to its exceptional durability. During the 2nd or 3rd century BCE, a large-scale production of hydraulic mortars began in the Gulf of Naples. This kind of hydraulic mortar was mixed with pozzolana, a pyroclastic deposit coming from the Campi Flegrei in the Gulf of Naples and was suitable for water-saturated structures and especially for harbor infrastructure. It seems that the maritime concrete was firstly used in fishponds of villae maritime owned by the Roman elite [1]. Notable harbors built with pozzolanic mortar include Baiae, Portus Iulius, Claudius' and Trajan's harbors in Ostia Antica, Cosa, Santa Liberata, Egnazia, Caesarea Palestinae (Israel), Alexandria (Egypt), Chersonissos (Crete), and Pompeiopolis (Turkey).

A key source on Roman harbor construction is De Architectura by Vitruvius. Roman engineers used to build a wooden formwork underwater which was filled with pozzolanic mortar. The technique most commonly seen in surviving harbor remains was intended for use with marine concretes. However, pozzolana was not limited only in the Italian peninsula, but it was exported out of Italy for the construction of harbor installations. One of the biggest harbours which was constructed with maritime pozzolanic mortar is the harbor of Caesarea Maritime in Israel[2]. In the case of Caesarea's harbour, a combination of techniques regarding the mortar manufacture was applied.

Hydraulic mortars mixed with pozzolana were not only used for the construction of harbours, but they were also used for the building of structures which supported further activities in the area of the harbours. The Well Cistern found submerged in San Felice channel in the northern Venice lagoon, dated to the 1st CE, was utilized to provide fresh water to the ships. The Well-Cistern was constructed with hydraulic concrete mixed with Phlegrean Pozzolan indicating that pozzolana was traded in the Venice lagoon, even though it was considered a peripheral area of the Roman empire[3].

It is unclear whether maritime mortar was widely used in Byzantine harbor construction. The ROMACONS project found no Byzantine harbors built with hydraulic mortar. Procopius of Caesarea refers to the construction of harbour facilities near Constantinople with the use of caissons (wooden formworks) filled with rubble. Hohlfelder saw this as hydraulic mortar[4], while Gertwagen believed in the past that the caissons were not filled with any kind of hydraulic mortar[5]. The Yenikapı jetty shows the use of wooden formwork filled with mortar, rubble, and ceramic sherds—suggesting limited use of maritime concrete in

1 Holhfelder and J.P. Oleson 2014.
2 Vola et al. 2011.
3 Dilaria et al. 2024, 23.
4 Hohlfelder 1988, 54-62, Hohlfelder 2024, 39.
5 Gertwagen 1988, 149.

the Medieval period[6]. Unlike Roman concrete, this mix used ceramic fragments as artificial pozzolana. Italian pozzolana reappeared in harbor construction under the Ottoman Empire in the late 18th and 19th centuries[7].

This review examines the historical development, material properties and durability concerns of maritime concrete in historic structures in the Mediterranean region. The need to protect and preserve these constructions that have historic value has led many researchers to study maritime concrete, to propose new compatible restoration materials. The study of several sites over the years has established that the hydraulic character of maritime concrete, due to the combination of air lime with pozzolanic materials, is responsible for its performance and durability[8]. The origin of the pozzolanic materials differs based on the location of the construction and their selection seems to be based on the required properties of each mortar/concrete. In recent research, scholars have utilized high-resolution surface and internal imaging, combined with chemical mapping, to characterize the microstructure in order to determine the connection of microstructural composition and the macroscopic durability in Roman Maritime Concrete[9] . The overall evaluation of the chemical, physical and mechanical characteristics of the samples demonstrates in each case the nature of the materials, their behavior in construction as well as their resistance to the very special conditions of their environment. Further research should continue to explore innovative materials and techniques to mitigate environmental degradation and ensure the longevity of coastal infrastructures. The analyses on maritime concrete have demonstrated that a significant number of chemical and mineralogical reactions occur in the mortar giving rise to new hydraulic products which keep the mortar resistant to water saturation and environmental erosion. The binder of the maritime concrete is composed of a micro crystalline compound known as C-A-S-H (Calcium Alumino-Silicate Hydrates). Another phase occurred in the maritime concrete is Al tobermorite which develops in the cementitious matrix and in the lime clasts. Moreover, zeolite microstructures occur in the pumice vesicles and the mortar fabrics[10]. Furthermore, recent research has indicated the precipitation of M-A-S-H (Magnesium-Aluminum-Silicate-Hydrates) in the maritime concretes which are promoted by seawater and the possible addition of combustion residues from organic matter[11]. Other scientific studies showed that Roman Maritime Concrete is characterized by high ductility and low permeability which are responsible for concrete's durability. This situation is formed by the calcium-sulfo-aluminate fibers embedded in a matrix which is composed of C-A-S-H and N-A-S-H phases[12].

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6 Ercan Kydonakis 2024, 141.
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How different are the natural hydraulic limes available in the European market?

1. Introduction and aims

Natural hydraulic limes (NHL) are binders widely marketed and used in sustainable construction and restoration due to their compatibility with traditional materials, higher breathability, and lower stiffness compared to conventional cements[1]. Notwithstanding, various authors dismiss their use because of their high compositional variability and unpredictable physical-mechanical behaviour, which may compromise the performance of their mortars and the correct preservation of the historic structures[2]. This criticism may be attributed to two main aspects:

1) In first place, the lack of rigor in the regulations governing NHLs, as the EN 459-1[3] standard does not establish strict chemical-mineralogical and physical-mechanical criteria[4], and classifies NHLs into 3 types based on their minimum compressive strength (MPa) at 28 days, using only the free lime ($Ca(OH)_2$) content as a distinguishing compositional criterion (≥35% for NHL2, ≥25% for NHL3.5, and ≥15% for NHL5). Consequently, there is significant uncertainty about their properties, making it difficult to predict their physical-mechanical behaviour, which is further complicated by the overlapping strength ranges (2-7 MPa for NHL2, 3.5-10 MPa for NHL3.5, and 5-15 MPa for NHL5).

2) In second place, the influence of the raw materials and manufacturing conditions (calcination temperature and duration, slaking) on the chemical-mineralogical composition of natural hydraulic limes[5], which in turns influences the setting and final performance of NHL mortars. This aspect particularly suggests that NHLs from different manufacturers may exhibit significant compositional and textural variations, even when assigned the same index.

In this work, natural hydraulic limes manufactured in 6 industrial plants from 4 different European countries from those shown in Figure 1 have been analysed in order to understand how variable the characteristics of these limes are as a function of the raw materials and manufacturing process used, with the final purpose of demonstrating that a more rigorous standardisation of this binder is needed. A total of 17 natural hydraulic limes (NHL2, NHL3.5, and NHL5) have been analysed by means of chemical (X-ray Fluorescence, XRF), mineralogical (X-ray Diffraction, XRD and quantitative analysis), and micro-textural (scanning electron microscopy, SEM) techniques.

2. Results and discussion

In all NHLs, the portlandite ($Ca(OH)_2$) content falls within the ranges established by the EN459-1 regulation, being 38-42% in the NHL2, 24-43% in NHL3.5 and 16-40% in NHL5. In some of the most hydraulic limes, the free lime content is much higher than the expected. A variable content of calcite was also

1 Lanas et al. 2004.
2 Copsey 2020.
3 CEN 2015.
4 Figueiredo, Ball, Lawrence 2016.
5 Parra-Fernández et al. 2024.

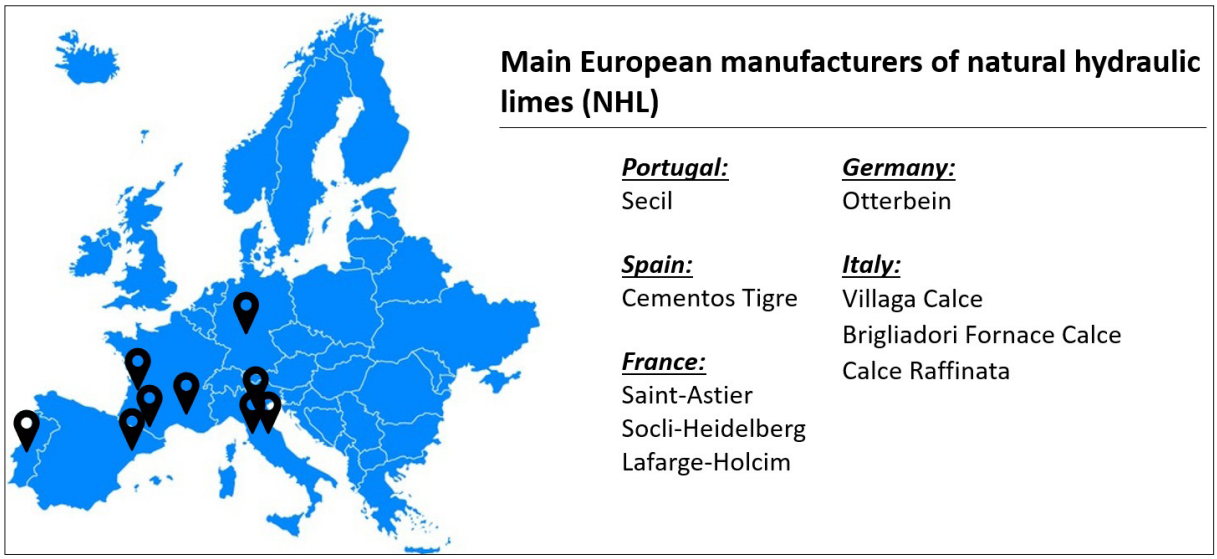

Figure 1 Locations of the main European manufacturers of natural hydraulic limes (NHL) today.

found, from 4 to 35% in each NHLs hydraulic group, suggesting: 1) different burning temperatures that may explain variable residual contents of calcite, and/or 2) re-carbonation of Ca(OH)2. The presence 7-11 % of spurrite (Ca5(SiO4)2CO3) in all NHLs manufactured in 2 of the 6 analysed plants clearly indicates reaction of re-carbonation inside the kiln, during the calcination step.
Only in two of the commercial varieties of NHLs, lime (CaO) and periclase (MgO) were found in very low amounts (<1% and <2%, respectively).
The predominant hydraulic phase in all limes is larnite (C2S), whose content is quite similar in all NHL2, ranging from 13 to 18%, but is more variable in NHL3.5 and NHL5. The majority of these limes, indeed, shows similar C2S contents than those found in NHL2, and only one or two of them reach 25%, in NHL3.5 and NHL5. Hatrurite (C3S) is also present in all samples in variable amounts (1-8%) more dependent on the commercial variety than on the hydraulic degree of the lime.
C3A was found as secondary phase (1-3%) in all NHLs, whilst C4AF (in amounts <3%) was found only in the limes with a Fe2O3 content >1%. Approximately 3-5% of hydrogarnet (Ca3Al2(OH)12) was detected in only one commercial variety of NHL2, NHL3.5 and NHL5. Gehlenite (Ca2Al(AlSiO7) and akermanite (Ca2MgSi2O7) were detected in amounts ranging from 1% (in NHL2) to 4% (in NHL5), but only in two of the commercial NHLs, showing a dependence on the manufacturing process and/or the raw material used.
Up to 7% of quartz (SiO2) was found in all NHLs, whilst other minor phases such as tridymite and cristobalite (both quartz polymorphs), wollastonite (CS), and magnesite (MgCO3) were detected only in one or two commercial varieties. Finally, small amounts (<0.5%) of sulphate phases such as bassanite (CaSO4·1/2H2O), and anhydrite (CaSO4) were detected in NHLs from 3 different manufacturers.
Regarding their microstructure, all the studied limes are formed by agglomerates of 10-30 µm composed of micrometric (<2 µm) calco-silicate particles. Their main differences lie in the proportion of uncalcined raw material fragments, as well as in the presence of phases with cubic/octahedral habits related to the hydrogarnet family, and lamellar particles that may belong to the Ca-AFm family.

3. Conclusions

This study highlights that the lack of rigour of the European standard on natural hydraulic lime causes significant differences between NHLs with the same designation, creating uncertainty about their performance. It was demonstrated that, even though the NHLs manufactured in six industrial plants throughout

Europe comply the European regulations established for this binder, a wide compositional variability exists among them mostly as a function of the manufacturing process. This encourages to carry out further studies on the specific fabrication steps and raw materials used in each analysed plant, to explain and justify such a huge variability of the NHLs available in the market, with the final purpose of encouraging and promoting a stricter standardisation for this binder.

Acknowledgements
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Ancient Mortars and Plasters in Roman Food Production Facilities

1. Introduction

Lime mortars and plasters, since ancient times fundamental elements of architecture, reflect technological achievements and the transmission of knowledge across different contexts. In recent years, numerous studies have demonstrated and confirmed that investigating the chemical and physical composition of these materials can offer insights into the choices made regarding raw materials and reveal enduring production techniques[1].

This study presents a preliminary contribution within the framework of a broader ongoing research project on Roman plasters from the Western Mediterranean, specifically from archaeological sites located in Spain and Italy, where structures dedicated to food production and storage were excavated. The function of these facilities was determined or confirmed thanks to the archaeological context and, when possible, also through organic residue analysis[2].

These installations are characterized by the presence of vats that came into contact with substances such as wine, oil, and/or fish by-products. The study is guided by the premise that the analysis of the mortar and plasters used to coat these vats provides information on construction practices with the objective of determining whether these mixtures were designed for specific functional and technological purposes.

While the broader research includes multiple archaeological sites and a larger dataset, the site of Cortijo del Canal, located in the Sierra Arana (in the territory of Granada), has been selected as the case study due to its representativeness for the analysis of production-related mortars and plasters.

2. Methodology

Thirteen samples were collected from within the Cortijo del Canal production area, specifically from spaces dedicated to pressing and liquid collection. More precisely, the site is organized into distinct areas: a press area with opus latericium, a floor paved with cocciopesto, and, directly below, a set of three vats where the liquid from the pressing process would be collected.

A multi-analytical approach was adopted, integrating petrographic, physico-chemical methodologies and archaeological study[3]. A detailed characterization of the plasters was conducted using a range of analytical techniques, including Optical Microscopy (OM), X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), and Ionic Chromatography (IC). These methods allowed to understand the type of raw materials used, production techniques and characteristics of the mixtures.

Special emphasis was placed on the determination of hydraulic indexes (HI)[4], given that the study focuses on building materials used in the construction of structures exposed to liquids and semi-liquid food

1 Columbu et al. 2017; Dilaria et al. 2023; Lezzerini et al. 2017; Miriello et al. 2010; 2021; Secco et al. 2018.
2 Pecci, Cau, Garnier 2013; Pecci, D'Andria 2014.
3 Dilaria et al. 2023; Lezzerini et al. 2017; Miriello et al. 2021; Secco et al. 2018.
4 Boynton 1980.

products, such as wine, oil, and fish by-products (e.g., garum, salted fish). Considering this, architectural elements like vats and presses likely required the application of specific durable building materials resistant to aggressive substances.
Statistical techniques were employed to analyze data on binder and aggregate percentages, chemical compositions and the HI of the binders.

3. Preliminary observations

The materials analyzed from Cortijo del Canal exhibit a relatively homogeneous composition, predominantly reflecting the local geological context and suggesting the use of locally sourced raw materials. The samples are generally coarse-grained and poorly sorted, with limited fine fraction. Cocciopesto is the main pozzolanic component, with its amount and form (powder or coarse) varying by architectural element: higher and finer in vats, coarser in floors, and absent in interior partition walls. The presence of soluble salts and secondary calcite indicates interactions with liquids over time and degradation processes. The hydraulicity index (HI) values also show limited variability, further supporting the material's uniformity.
Unlike the case of Cortijo del Canal, where hydraulicity index (HI) values are high and consistent across all samples, other cases—such as the fish production installations presented in Girimonte et al. (in press)—exhibit certain differences. This contrast highlights that HI can vary potentially due to intentional technological choices or degradation processes that alter the original material properties. Consequently, it is essential to assess each case individually, taking into account the specific context in order to understand the material's transformation over time. Furthermore, the evaluation of the conservation state of each sample, combined with the analysis results, provided insights into the presence of probable degradation products and the factors influencing their formation.
This study seeks to advance our understanding of ancient construction technologies by investigating raw materials, characteristics and technological evolution of Roman mortars within specific functional contexts.

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From ashes to architecture: the use of pozzolan in Roman Mortars

1. Introduction and research aims

Technological advances throughout history have been achieved through the wise and intensive use of available georesources. Mortars are composite geomaterials consisting of hydraulic or aerial binder, aggregates, and additives that react with binder and undergoing modifications during setting[1]. These geomaterials are of particular interest due to their great production by Romans. M. Vitruvius Pollio (1st century B.C.) in De Architectura, and Pliny the Elder (23-9 A.D.) within his Naturalis Historia described the romans building art: roman craftsmen used to combine lime and pozzolan, allowing mortars to become hydraulic, hardening underwater and increasing their mechanical strength[2]. The use of pozzolan marked a great advance in construction technology: ancient pozzolanic mortars testify the high technological quality achieved by Roman construction workers, due to their 'excellent state' of preservation in every environment. The original pozzolan is pulvis puteolana, a volcanic sand from the Phlegraean Fields area. As reported by Vitruvius, this was considered a "prodigious powder," found across a wide region, from Baiae and Cumae to Vesuvius and Sorrento Peninsula. The term "puteolana" was first used by Pliny, who located the origin of the material in the ancient city of Puteoli (modern-day Pozzuoli, Naples). Geologically, pulvis puteolana is an incoherent facies related to the Neapolitan Yellow Tuff (NYT) eruption, which occurred approximately 15.000 years ago[3-4]. The Romans founded one of the greatest empires in history, conquering the Mediterranean area and half of Europe. Traces of their presence can be seen through buildings, roads, aqueducts, temples and monuments. From an architectural perspective, the Romans inspired many populations, both past and present. Their ability to build monuments starting from simple geological materials and transforming them into more complex and durable ones has long attracted the interest of researchers. The study of Roman mortars is of exceptional importance to understand their construction technology as the extraordinary preservation state of these geomaterials proves the very high technological skills of these builders. For this reason, mineralogical, petrographic, chemical, and microstructural characterizations have been carried out on mortars from various archaeological sites located in the Phlegraean Fields area (Figure 1). These include ancient Roman structures built in subaerial environment and later submerged by seawater, as well as structures in prolonged contact with water (e.g., thermal baths and cisterns).

2. Geological and archaeological background of the investigated sites

The investigated archaeological sites are located within the Phlegraean Fields volcanic district (Campania region, Southern Italy) which, along with Somma-Vesuvius, represent one of the two most important and still active Quaternary volcanic systems of the Mediterranean area. Phlegraean volcanic activity is characterized by explosive eruptions that produced large volumes of pyroclastic deposits, plus sporadic ef-

1 Moropoulou, Bakolas 2005.
2 Collepardi 2003.
3 Deino et al. 2004.
4 Montesano et al. 2022.

Figure 1. Map of Phlegraean Fields area with locations of Baia Thermal Complex (orange star), Piscina Mirabilis (yellow star), Anfiteatro Flavio (green star) and Dragonara Cave (red star).

fusive events represented by lava flows and domes[5]. Piscina Mirabilis (yellow star in Figure 1) represents one of the most popular destinations for European travellers in Italy. Always recognized as cistern, the site is considered as part of the villa of Lucullus basing on Plutarch's text, to supply water to the military fleet stationed at Miseno, or to connect the area to the Serino aqueduct according to Emperor Nero's intensions[6]. The Thermal Complex of Baia (orange star in Figure 1) represents one of the most important archaeological sites of Campania region. Thanks to the several thermal springs, the city of Baia was the holiday resort of the Roman aristocracy. The Dragonara Cave (red star in Figure 1), from the latin "tracon" which means "rocky", is a large Roman cistern dug into the tuffaceous promontory. The Anfiteatro Flavio is one of the largest amphitheatre arenas of the Roman Empire, third in size only to the Colosseum in Rome (Lazio, Italy) and the amphitheatre od Santa Maria Capua Vetere in Caserta (Northern Campania region).

3. Results

Studies of ancient Roman mortars from the abovementioned archaeological sites[7-8-9-10] revealed a consistent use of locally sourced materials, primarily volcanic tuff from the Phlegraean Fields Area, combined with hydrated lime and ceramic fragments. Advanced analytical techniques such as Polarized Optical Microscopy (POM), X-Ray Powder Diffraction (XRPD), Field Emission Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (FESEM-EDS), Mercury Intrusion Porosimetry (MIP) and Thermal Analysis (TA) were employed to investigate their mineralogical, chemical and microstructural

5 Morra et al. 2010.
6 Borriello, D'Ambrosio 1979.
7 Rispoli et al. 2020.
8 Rispoli et al. 2019.
9 Rispoli et al. 2024.
10 Montesano et al. 2022.

properties. Mortars exhibit hydraulic characteristics, demonstrated by the presence of reaction rims and amorphous calcium-aluminium-silicate-hydrate (C-A-S-H) gel, along with calcite, Al-tobermorite and gypsum resulting from lime-pozzolana and lime-ceramic reactions, contributing to the mortar strength and durability. The findings confirm Roman expertise in selecting and combining materials to optimize mortar performance, providing valuable insights for future restoration and conservation efforts by revealing the technical skills and mix designs that ensured the longevity of these historic structures.

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Herodian Construction Techniques and Building Materials: Analysis of Mortars, Plasters, and Concrete in King Herod's Architecture in Judaea

This study investigates how King Herod (37-4 BCE) strategically adopted and adapted Roman material technologies across Judaea by analyzing the composition and application techniques of mortars, plasters, and concrete in his monumental architectural program[1]. Herod founded entire cities such as Caesarea Maritima[2] with its massive port, while his extensive building program throughout Judaea included palaces, temples, fortresses, settlement sites, and entertainment structures such as theaters and hippodromes. We sampled mortars, plasters and concrete materials in Herod building projects from Herodian Caesarea (Figure 1), Paneas[3], Herodium (Figure 2), Jericho[4] and Alexandrium[5]. The samples were analyzed using optical microscopy (ZEISS SteREO Discovery.V12), polarized light microscopy, X-Ray Fluorescence (Bruker i5), Fourier transform infrared spectroscopy (FTIR), X-Ray Powder Diffraction with quantitative phase analyses, and scanning electron microscopy with EDS microanalysis (SEM-EDS).

Our analyses reveal distinctive signature patterns in material formulation and application methods, illuminating Herod's sophisticated integration of Roman engineering innovations within the local building traditions of first-century BCE Judaea. For example, Herod's masons increased the use of lime in mortars, and were the first in Judaea to systematically use wood ash as an active additive in water facilities plaster and mortars. Another innovation was one time use of pottery sherds evidenced in the plaster of an installation at Herodium dated to the later days of the King[6]. This recipes with the addtives of pottery sherds and ash, will become dominant in the coming centuries. An additional combination of mixtures witnessed in a variety of functions in the Herodian constructions–e.g., in mortars and in grouting at walls in Herodium–is based on lime and imported gypsum. Except for Caesarea Maritima, the use of imported gypsum—a material not locally available—ceased in Judaean construction after Herod's reign. Caesarea was the only site in which volcanic ash was detected in Herod's building projects (Figure 3)[7]. Even at other Herodian buildings, in which the Roman opus reticulatum technique was utilized, namely at Paneas (Figure 4) and Jericho, his architects\masons used local ingredients for the concrete core of the walls. These innovations in building materials represent just one aspect of Rome's comprehensive influence on Herodian architecture, which also encompassed the adoption of Roman building techniques (opus reticulatum), Roman architectural typologies (theaters, hypocaust systems in bathhouses), and decorative elements (modillion cornices, opus sectile floors, stucco coffered ceilings). These material innovations represent a calculated technological diplomacy, as Herod simultaneously demonstrated cultural sophistication to Rome while showcasing his privileged imperial connections to local populations through the tangible medium of architectural materials. This pioneering multi-site analysis of building materials across Herod's major architectural projects—spanning Caesarea Maritima, Paneas, Herodium, Jericho, and Alex-

1 Richardson 1996.
2 Porath 2008, 1656–1665.
3 Bar-Nathan and Snyder 2019.
4 Netzer 2001.
5 Netzer 2006; Roller 1998.
6 Porat, Chachy, Kalman 2015, 109.
7 Oleson and Branton 1992; Secco et al. 2022.

Figure 1. The northern wall of Alpha Vault in the Augusteum at Caesarea Maritima (b.6: the concrete casting and the ashlar wall).

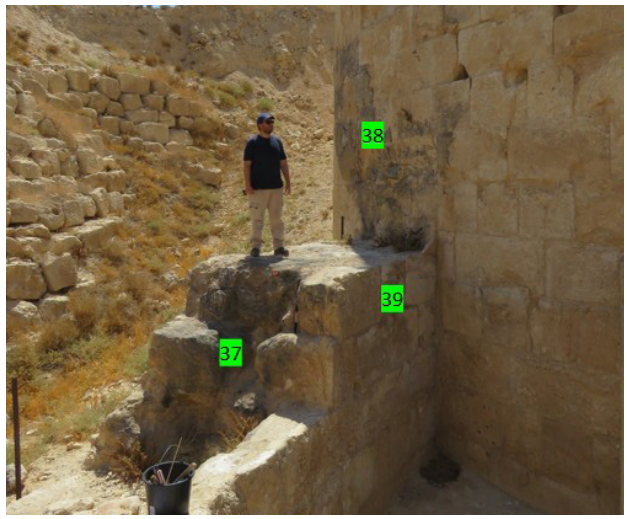

Figure 2. The fortification and the eastern tower at Herodium (b.37: core mortar; b.38: grouting; b.39: joint mortar).

Figure 3. The wall in the western part of the lower terrace of King Herod's Promontory Palace at Caesarea Maritima (b. 23: core mortar).

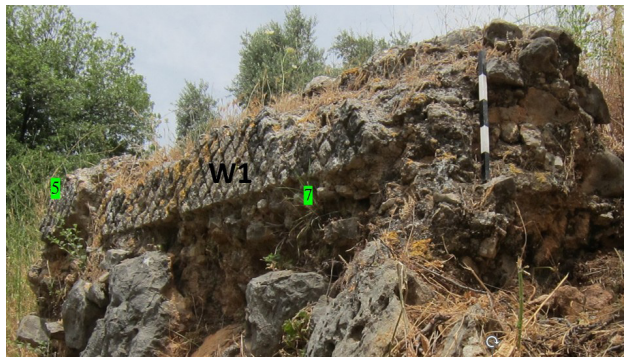

Figure 4. The Opus Reticulatum wall at Paneas (b. 5: core mortar; b. 7: foundation mortar).

andrium—provides unprecedented insights into regional patterns of technological adaptation. Our findings reveal how bonding materials compositions were strategically adapted to specific architectural functions and environmental conditions while documenting the selective transfer and regional adaptation of Roman material technologies to the eastern Mediterranean. The systematic variations in mortar, plaster, and concrete formulations across these sites provide valuable insights into the technical sophistication of Herodian construction practices and illuminates broader patterns of technological diffusion in the early Roman period.

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Resin and pitch in Roman plasters of food production vats: a technological practice?

1. Introduction

Food production installations in Roman and Late Roman times are characterized by the presence of vats. This is the case especially for installations devoted to the production of wine, oil and fish by products (e.g. garum).

These vats were usually coated with lime plasters, that were needed to waterproof them and to allow the storage of the liquids involved in the production of the different substances, for shorter or longer periods.

Although the function of the different installations can be sometimes recognized by studying their organization and archaeological characteristics, organic residue analysis has demonstrated to be a fundamental tool to verify the archaeological hypothesis. In fact, it has allowed to identify substances that do not always correspond to the expected ones and has helped to recognise possible re-uses (or multiple uses) of the installations (Pecci et al. 2013).

Therefore, organic residue analysis of the installations vats is usually aimed at understanding the substances produced. However, these analyses have also provided information on a possible technological practice in the making of the plasters.

2. Methodology

Samples have been collected from vats of Roman and Late Roman production installations located in Italy and Spain.

They were cleaned and subsampled in the laboratory and two extractions were carried out following Mottram et al. (1999) or Correa Ascencio and Evershed (2014) to obtain the lipid extract, and Pecci et al. (2013b, 2020) to identify residues compatible with wine production.

The extracts were derivatized and analysed with gas chromatography coupled with mass spectrometry (GC-MS).

The analyses were carried out at the Universities of Siena and Barcelona, using the installations of the CIADS in the first case and the Laboratorio de Arqueología and the CCiT-Ub in second.

3. Results

The analyses have allowed to identify the content of the vats and therefore confirm the function of the production installations. In some cases, the results confirmed the archaeological hypothesis and in others they suggested different interpretations from the ones expected.

An interesting datum was the identification of resin and sometimes pitch biomarkers in several vats. These substances were commonly used in Roman and Late Roman periods to coat dolia and amphorae where food and beverages were produced, stored and transported.

The aim of coating the pottery vessels was surely to waterproof them, but likely also to preserve the content and in some cases also to give flavour (especially in the case of wine).

The results of the organic residues analysis of the vats' plasters suggest that maybe also in the first stages of the production of these substances, when they were still stored in the production installations vats, resin or pitch could have been used to achieve the same objectives. For this, resin or pitch could have been mixed in the plasters, revealing a specific technological practice that could characterize the making of plasters of production installations vats.

4. Acknowledgments
This work is part of the activities of the I+D project RACAMed II (PID2020-113409GB-I00), the ERAAUB Research group (2021 SGR 00696), the Instituto de Arqueología de la Universitat de Barcelona (IAUB), the INSA-UB María de Maeztu Unit of Excellence (CEX2021-001234-M) and the Department of Studi Umanistici of the Università della Calabria. G. Girimonte has a PhD FI-SDUR 2022 (5635I22) contract.

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Insights on hydraulic phases in mortars from ancient Roman aqueducts

1. Introduction

Ancient Roman aqueducts are infrastructures that leave us astonished because of their technological level and their persistence. For the city of Rome, eleven main aqueducts were built during the Roman civilization, the most ancient (Aqua Appia) being built in 312 BC and the most recent (Aqua Alexandrina) in 226 AD[1]. Not only archaeological remains are still visible to testify the majesty of these architectonic structures, but two of these aqueducts, Aqua Virgo (19 BC) and Aqua Traiana (109 AD), are still working. Among the different factors that influenced their persistence, the building materials employed play a crucial role. Historical sources, among which Vitruvius' De architectura, report some information about the materials employed at the time to produce durable mortars. To obtain hydraulic mortars, ancient Romans added materials with pozzolanic behavior to the lime binder[2]. These materials were both natural, including volcanic ash, pumice and tuff, and artificial, i.e. ceramic fragments, as reported in numerous archaeometric studies that have been conducted on ancient Roman mortars[3].
Archaeological and historical information exist in the literature about this constructions[4], but very few document the composition of these specific materials. The aim of this work is thus to characterize the mortars and plaster from the inner ducts of ancient Roman aqueducts built for the city of Rome.

2. Materials and Methods

2.1 Mortars and renders from ancient Roman aqueducts

Samples of mortars and plasters have been collected from the inner ducts of some of the ancient Roman aqueducts built for the city of Rome (Table 1). The sampling was conducted thanks to the permission of Sovrintendenza Capitolina ai Beni Culturali, Soprintendenza Speciale Archeologia, Belle Arti e Paesaggio di Roma, Parco Archeologico dell'Appia Antica and Acea Ato 2. Both original and restoration mortars have been collected, with the support of archaeologists.

2.2 Analytical techniques

The characterization of samples has involved optical microscopy (OM), X-ray powder diffraction (XRPD) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS). To determine the hydraulicity of the binder, samples have been sieved and the fraction smaller than 63 µm underwent thermogravimetric analysis (TGA). High resolution field emission scanning electron microscopy (HR-FESEM) and pair distribution function (PDF) analysis on diffraction data obtained at the European Synchrotron Radiation facility (ESRF) have been performed on selected samples that presented an amorphous binder rich in Si and Al.

1 Pace 2010.
2 Torraca 2009.
3 Rispoli et al. 2024.
4 Ashby 1935.

Structure	Dating	Number of samples
Aqua Virgo	19 BC	17
Aqueduct Y	unknown (Roman)	3
Aqua Claudia	38-52 AD	4
Anio Novus	47-52 AD	5
Aqua Traiana	109 AD	47
Sette Bassi aqueduct	2nd century AD	2
Villa dei Quintili aqueduct	2nd century AD	2
Aqua Antoniniana	215 AD	2
Aqua Alexandrina	226 AD	25

Table 1. List of aqueducts involved in the present study, dating of the original structure and number of samples collected.

3. Results and discussion

3.1 Mortars characterization

Characterization through OM, XRPD and SEM-EDS allowed the identification of materials with pozzolanic behavior, both natural and artificial, in all the samples investigated. The provenance of the natural pozzolanic materials is generally compatible with the geological setting of the area where each specific aqueduct is located, being Rome and its surroundings rich in volcanic rocks belonging to Colli Albani and Monti Sabatini volcanic districts. The most relevant outcome is related to the binder. Some samples coming from Aqua Traiana and Aqua Virgo do not show the presence of calcite in the binder, that can be described as amorphous, rich in Si and Al. Determination of CO2/H2O ratios from TGA on the binder fraction highlights a higher degree of hydraulicity for the amorphous binders, respect to other samples in which hydraulic phases are accompanied by calcite.

3.2 HR-FESEM and PDF analysis

To better characterize the amorphous binder, HR-FESEM has been used for micro-morphological and micro-chemical investigations. Needle-shaped formations of nanometric dimension have been found in some samples, assessing the presence of a blade-like cementitious binder .

PDF analysis has been chosen to determine the local order within the amorphous binder. The analysis has been performed on the fraction smaller than 63 μm. The diffractograms have been interpreted using EVA software, to determine the presence of eventual crystalline phases that are residues of the aggregate. Then the data have been analyzed using PDFgui software, which allowed subtracting the crystalline phases from the signal, to isolate the contribution of the amorphous phase. The isolated peaks have been compared with the literature, showing that the binder is compatible with calcium-sodium/potassium aluminosilicate hydrate (C-(N,K)-A-SH), with a lack of Ca2+ in the average local structure. Moreover, a nanocrystalline phase, similar to phillipsite, is present in some of the samples.

4. Conclusions

The archaeometric investigation of mortars and plasters from ancient Roman aqueducts not only allowed a deeper knowledge about the technological level reached in the realization of hydraulic mortars, but also the discovery of a highly hydraulic binder with an amorphous binder similar to modern phases found in cements. The characterization of this binder can be helpful also for the understanding of amorphous

phases formation and stabilization. For this reason, the project DAPHNE- "Deciphering the formation of AmorPHous binders in ancient RomaN mortars for modErn applications" (MSCA Postdoctoral Fellowship) will investigate the factors that allowed the formation of this peculiar binder.

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Assessing Construction Techniques through Minero-Petrographic Analysis of Roman Mortars: Insights into Imperial Economic Investments in Building Projects

1. Introduction

The manufacturing of mortars can be considered such an art that began in historical times and reached significant advancements, wide diffusion and innovation in the production, particularly during the Roman Empire. Roman craftsmen used to combine lime with pozzolanic material to produce hydraulic mortars, allowing underwater hardening and increasing their mechanical strength[1-2].

1.1 The Economy of Roman Imperial Architecture project

This study is part of the ongoing Economy of Roman Imperial Architecture project, which aims to assess the nature and extent of imperial investment in Rome's construction industry during the 2nd to 4th centuries CE through qualitative and quantitative evaluations of masonry and mortars from imperially sponsored, functionally and chronologically compatible buildings such as baths, domus and basilicae. The research was funded by the Rome Transformed project (ERC grant agreement No. 835271) and by Newcastle University PGRAs research funds [3-4].

The masonry data capture process included visual inspection, structural analysis, and 3D laser scanning of the structures to evaluate their function, chronology, and conservation state. Moreover, an in-depth assessment of the quality, technical and dimensional characteristics was also performed, examining factors such as brick size, type and quality, the presence of pointing or surface reworking, and determining the height of modules. Then, mortars from structurally compatible and chronologically coeval walls were samples and analyzed (Figure 1).

1.2 Analytical techniques

Petrographic analysis was carried out on thin sections via polarized light microscopy (PLM). Furthermore, microstructural and chemical analyses of the investigated mortars, aimed to determine major elements chemical composition of binder and the lime lumps, were carried out by Field Emission Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (FESEM/EDS). Furthermore, FESEM-EDS analyses were performed on areas with homogeneous appearance and with spots of 10 µm for measuring hydraulicity index (HI) of binder and lime lumps. According to[5], the semiquantitative measure of HI accounts for the (SiO2 +Al2O3 + Fe2O3)/(CaO + MgO) ratio.

1.3 Preliminary results and outcomes

Preliminary results showed that all the investigated mortars are characterized by a lime-based binder with a cryptocrystalline and micritic texture in different proportions. The binder fraction also contains

1 Miriello et al. 2015.
2 Lezzerini et al. 2018.
3 Haynes et al. 2024.
4 Haynes et al. 2023.
5 Boynton et al. 1996.

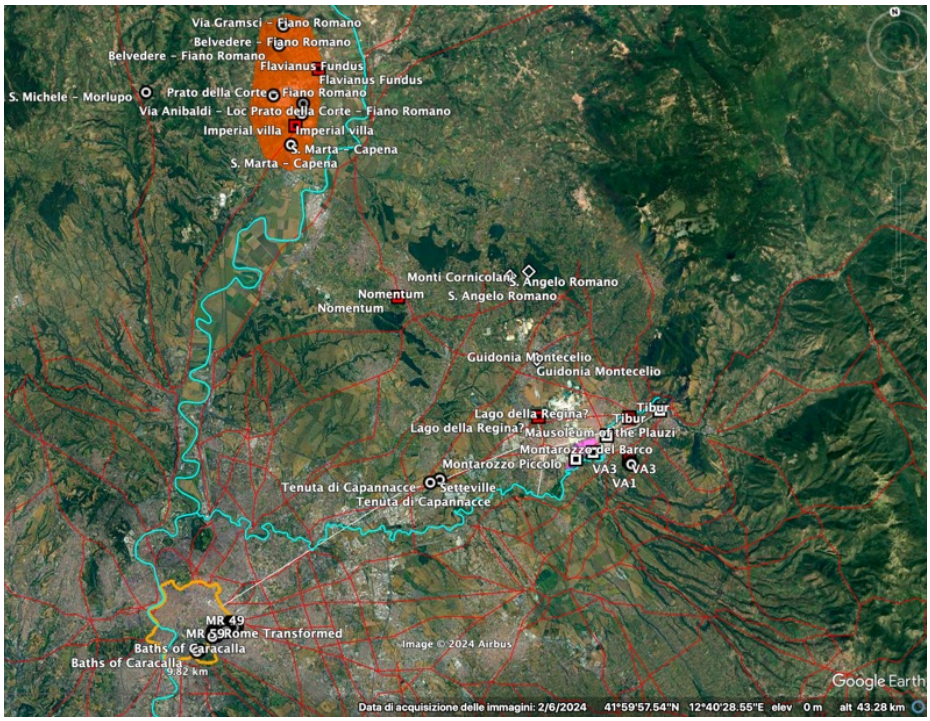

Figure 1. Map of sampling sites in the Rome area.

lime lumps. The aggregate fraction mainly consists of mm- to cm-sized volcanic fragments (red and black scoriae), showing reaction rims and secondary carbonation process evidences. The composition of the volcanic aggregate is consistent with ultrapotassic products of the Roman Magmatic Province, likely originating from the volcanic district of the Alban Hills[6]. This provides important insights into the main area of supply of these aggregate, located in the proximity of the buildings.

The obtained data provided interesting preliminary insights about the composition of the mortars, as well as their likely production techniques. These results are pivotal to assess the economic investment required for the sourcing of raw binding and aggregate materials needed for the construction of imperial buildings. The examination of the mortar composition and manufacturing methods by using petrographic and microstructural techniques and the identification of raw material could reveal trends in material sourcing, technological choices, and possible cost-saving strategies. By linking these findings to supply locations and construction practices, the study assess serve as a proxy for measuring the economic dimension of imperial construction projects by revealing the material investment embedded in Rome's monumental architecture. This makes the study important for reconstructing the economic strategies underpinning the Roman Empire's building programs. The use of specific raw materials could reflect trend related to cost-saving measures, such as increasing the use of less expensive aggregates in the mortar mixtures during times of significant imperial expenditure or indicate practices among imperial contractors aimed at either cutting costs (if their work was mandatory) or increasing profits by conserving resources. The proposed model of mortar analysis serves as a versatile tool applied differently to public and private architecture by tailoring the interpretation of material data to the scale, funding source, and socio-economic context of the building projects, focusing on one hand to the large-scale economic investment linked to imperial projects, on the other emphasizing socio-economic distinctions in the local construction practices.

6 Peccerillo 2005.

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First data on the raw materials and technical features of Arab-Norman mortars in Palermo: minero-petrographic analysis of the materials from the Uscibene Castle (12th century AD)

1. Introduction

The architectural style referred to as "Arab-Norman" is uniquely associated with the Sicilian urban centers of Palermo, Cefalù and Monreale and is characterized by the harmonious amalgamation of two quite different "architectural features": the Arab-Muslim and the Norman-Catholic. This exceptional synthesis culminated in the creation of remarkable edifices with intricate geometric patterns, mosaics, and monumental arches, creating cultural interchange and coexistence of the two styles during the medieval period [1-2]. In 2015, the UNESCO World Heritage Committee declared the Arab-Norman itinerary of Palermo a "World Heritage Site", thus including it in the World Heritage list. The Uscibene Palace complex serves as one of the "recreational venues" of the Norman monarchs, situated in the western periphery of the city of Palermo, with its construction tracing back to the 11th century. This edifice is positioned in proximity to a water source (Scibene spring), and was most likely built over an antecedent Arab structure within the confines of the Genoardo park (the “paradisiacal garden” that surrounded the city). The building consists of two levels: the lower level accommodates the principal hall, specifically a “trilobate iwan,” which is open on one side and features three niches. The upper level encompasses chambers that are adorned with cross vaults, serving various purposes, as well as the chapel, which was likely appended during the Norman epoch, albeit it has been substantially altered due to extensive restoration efforts undertaken in the 1920s.

2. Materials and Analytical techniques

Since 2021, the Soprintendenza BB.CC.AA. of Palermo, in collaboration with the Regional Archaeological Museum “A. Salinas,” has embarked on an extensive restoration initiative for the monumental complex, necessitating the execution of a suitable quantity of targeted diagnostic investigations.
Representative mortar samples (with different functions of use) were taken from the monumental complex under study, following multiple collaborative on-site assessments. Specifically, the specimens were taken from the most significant chambers: the chamber featuring a Roman vault, the Fountain chamber, and the Chapel. These included bedding mortars, plaster mortars and decorative relief mortars. All specimens underwent minero-petrographic analyses using X-ray powder diffraction (XRPD), optical microscopy (OM) and scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS).

3. Preliminary results and outcomes

Results highlighted the use of different recipes in relation to both the anticipated timeframe of mortar application and their specific functions. All mortars were derived from locally sourced materials; howev-

1 Montana et al. 2016.
2 Montana et al. 2018.

er, there exist marked differences between those utilized during the Middle Ages and those produced in subsequent centuries, during which considerable modifications were made to the original structure. Concerning the bedding mortars, the notable use of magnesian lime binders combined with aggregates derived from the milling of Pleistocene biocalcarenites (excavated locally to build the factory) during the Middle Ages was particularly emphasised; while, in more recent times (eighteenth century), the aggregate used for making the mortars comes from riverine alluvial deposits taken from the coastal strip east of the city walls[3-4]. Very peculiar is the discovery of a thin layer of wall covering made of magnesian lime and ash, placed between the anchoring layer and the levelling layer of the plaster, certainly of early medieval manufacture, serving the purpose of safeguarding the wall against moisture (Figure 1).

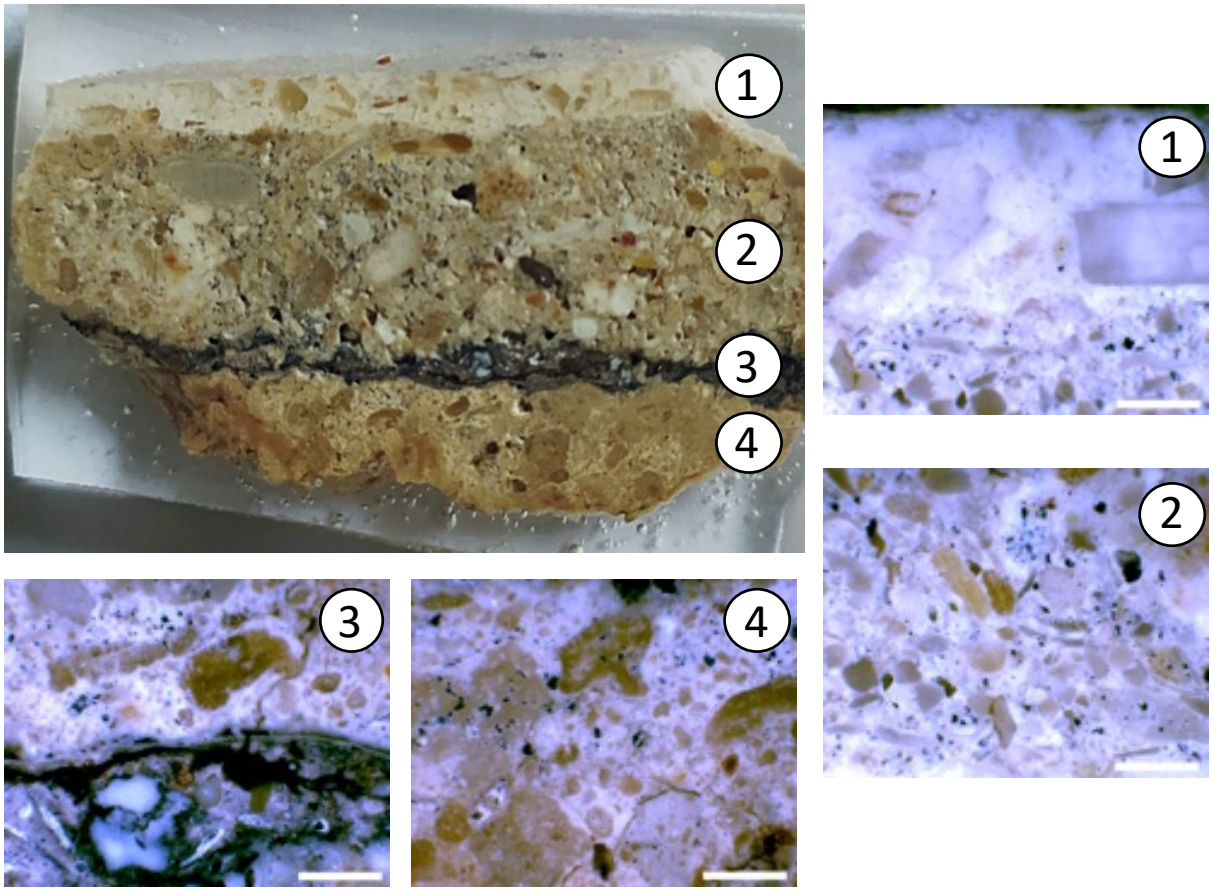

Figure 1. Cross-section of a representative mortar sample and related images in reflected light microscopy (scale bar=0.5 mm): 1) finishing layer; 2) leveling layer; 3) embedded ash layer; 4) anchoring layer.

Another noteworthy discovery pertains the decorative relief mortars (to create the Muqarnas) present in the "Fountain room" which are made with a mortar (very poor in aggregate) and a binder consisting of a mixture of gypsum and magnesian lime, or, only magnesian lime (pleated vaults). The acquired data, in addition to providing a novel and previously undocumented perspective regarding the manufacturing techniques of medieval mortars in Palermo, provide essential insights for the strategic planning of restoration intervention.

3 Randazzo et al. 2015.
4 Randazzo et al. 2020.

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Hadrianic concrete, a Roman archetype. Archaeometric characterization of construction materials from the Mausoleum of Hadrian, Rome

After 2000 years, Roman structures continue standing today as enduring symbols of a glorious past. Scientific studies have attempted to understand their exceptional resilience, in the hope that they might inspire and contribute to modern construction. Such research approaches can be used to formulate more sustainable and resilient building materials, to mitigate the well-known durability problems associated with contemporary buildings[1]. In this paper, the authors present ongoing research promoted by the University of Notre Dame, in collaboration with the University of Padova, which made possible an extensive characterization campaign of mortars and concretes used for the construction of the Mausoleum of Hadrian in Rome, a monumental construction dating to the 2nd century CE[2]. This robust monument, renowned for its imperial symbolism, consists of a massive concrete drum built on the bank of the Tiber River, dominating the Roman skyline. Emperor Hadrian's builders are commended for their attention to detail, from the careful selection of the building materials to the mortar recipes adopted which all together favoured a series of reaction chains, contributing significantly to the mausoleum's immense structural strength. This study, framed by a broader research project related to the architecture of the mausoleum, aims to document, analyse and characterize ancient Roman construction material, particularly mortars and stone rubble for opus caementicium (caementa). Additionally, the project examines the building construction techniques and parametrizes its formulation recipes.

More than 20 concrete and mortar samples were collected from different areas of the building dating to its original construction. Materials were subjected to an extensive characterization program aimed at tracking the provenance of raw materials and unravelling the microchemistry of the pozzolanic binders responsible for the longevity and durability of the structure. A multi-analytical approach was adopted, employing several analytic techniques such as Transmitted Light Optical Microscopy (TL-OM), X-Ray Powder Diffraction (XRPD), Scanning Electron Microscopy combined with Energy Dispersive Spectroscopy (SEM-EDS) and X-Ray Fluorescence (XRF), to characterize the petrographic, mineralogical and chemical composition of the building materials. The analysis was carried out in a 3-step process: binder-aggregate analysis of the bulk mortars via TL-OM, XRPD and SEM-EDS; microanalysis of the separated binder via XRPD; and finally, analysis of the caementa using petrographic and bulk-rock chemical characterization via TL-OM and XRF. In each category different groups of samples with similar compositions were observed and associated to determine their petro-mineralogical and microchemical composition and to identify any alterations and/or subsequent additions.

The statistical data acquired for all samples were interpreted to obtain conclusive results, showing the formation of cementitious reaction products even after the formation of the primary hydration phases. The long-term pozzolanic reactions further confirm the authenticity of the construction material used in Hadrian's mausoleum. A microchemical analysis using SEM-EDS shows the different stages of these

1 Secco et al. 2019.
2 Vitti 2014.

reactions, confirming the evolution of the high-quality Roman mortars and binders. The bulk mortar and separated binder analyses revealed significant occurrence of amorphous calcium aluminosilicate hydrate (C-A-S-H) gels in the binding matrices, as well as long-term microcrystalline hydration products, such as strätlingite[3]. The presence and location of these products within the cement matrices enhance the adhesive properties with the aggregate fraction, playing an important role in the increased strength of the structure over thousands of years. Regarding provenance, the analyses revealed a well-considered selection of construction materials, primarily of local origin. Colli Albani formations were extensively exploited for the sourcing of Pozzolane Rosse and Pozzolane Nere, used as aggregate for lime mortars, along with the extraction of caementa for the preparation of opus caementicium. The concrete samples collected from the mausoleum show the varying presence of Peperino (Lapis Albanus), Tufo Lionato and Leucitite as caementa, sorted by using the rocks with a lower bulk density in the higher part of the mausoleum. Consequently, Leucitite was primarily identified in the foundational casts of the building, contrary to its popular use as a paving stone during the Roman era. The choice of stones used for different purposes within the mausoleum gives further insight into the construction techniques adopted by Hadrian's architects and engineers.

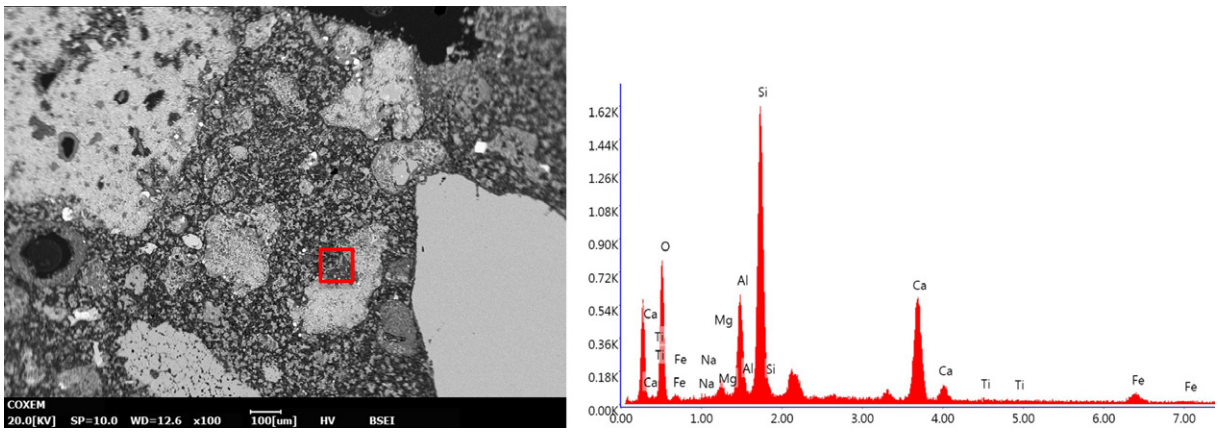

Figure 1. Back Scattered Electron (BSI) image and related EDS microanalysis of a decalcified matrix, indicating the formation of C-A-S-H gel and strätlingite.

This study highlighted the ambitions and risks undertaken by Roman builders to formulate construction materials that have survived millennia. Additionally, it provides a basis for further analysis to quantify variations in the quality of the mortar recipes among different structural and non-structural parts of the same building, aiding in identifying the level of design of mortars in this monumental construction. The mortar formulation recipes using pyroclastic additives has proven to contribute to reduced carbon emissions, producing para- and micro-crystalline cementitious compounds over long periods of time, enhancing durability in seismically active regions, and extending the service life of environmentally sustainable buildings. Therefore, this characterization study can inspire experiments with modern derivatives of ancient construction materials, to produce advanced and sustainable building materials following ancient Roman methods and techniques. The analyses can also be useful for the development of appropriate restoration methods and for the conservation of ancient Roman buildings.

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3 Seymour et al. 2023.

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Understanding of Materials and Techniques of Baroque Stuccoes and Their Repair

1. Introduction

Mortars used for stucco decoration of exteriors and especially interiors in the 17th and 18th centuries changed quite significantly composition compared to the Renaissance buildings and their plastic architectural features in the Czech territories. Stuccoes became more prominent in relief, which was made possible by the use of gypsum allowing for the firm support of various modelled shapes. The stucco decorations were carried out by craftsmen that were coming from the region of the great lakes of Como and Lugano. At the time it was an established practice with a tradition to hire an "Italian" craftsman for high-quality artistic decorations[1].

The study focuses on the characterisation of mortars and description of individual layers used to model and build the stucco decorations and compares three different case studies executed at similar time in the last quarter and at the end of the 17th century. The aim of the study is to understand the applied materials, construction techniques and final surface finishes with regard to the conservation and repair of stucco decorations.

2. Materials and structure of stuccoes

2.1 Case studies

Decorations of the Great Hall of Červená Lhota Castle (CL; carried out by I. Cometa around 1680), the Ground Halls of Kroměříž Castle (KC; B. Fontana, between 1690 and 1693), and the Corridor of Angeles at Uherčice Castle (UC; B. Fontana, after 1692) are compared in this study[2]. Particularly, the multi-layered structure and the materials used in the modelling of high-relief fruit and phytomorphic forms are compared here.

2.2 Materials and methods

Polished thin-sections were prepared from the samples and were characterised by means of optical microscopy (PLM) and scanning electron microscopy with energy dispersive spectrometer SEM-EDS. Another part of the sample was gently crushed and sieved. The binder-rich portion under 63 µm was ground to analytical fineness and analysed by means of Thermal Analysis (TA) and powder X-ray Diffraction (XRD). The proportion of insoluble residue (aggregate) was determined by dissolving the sample in 8% solution of hydrochloric acid. Samples containing gypsum had to be dissolved in boiling hydrochloric acid (1:3) for about 2 min. Presence of organic additives was analysed using nano-liquid chromatography with an ESI-Q-TOF Maxis Impact mass spectrometer.

1 Rampazzi et al. 2008.
2 Válek et al. 2020, Uccelli et al. 2022.

2.3 Characterisation of mortars - comparison

The stucco shapes are made from a core mortar, which is used to model the shapes with relatively final precision. The core mortar is covered by a 2–15 mm thin layer of a finishing mortar by which all the fine details are modelled on the surface. The core mortar structure varies based on the modelled shape. Larger statues have it composed of a gypsum-rich core applied on iron and subsequent layers of lime-gypsum-sand mortar used in layers to build up the desired mass and shape. The comparison here focuses on smaller shapes which are built without anchors.

The comparisons of the mortar compositions is given in Table 1. There are clear similarities in the proportions of the individual layers and the stucco structures. The finishing layer is made of the top-quality lime, which was locally available and fine sand. The core mortar is always based on a lime-gypsum mixture. Interesting differences are found in the processing of the binders, which leaves traces in the form of binder related particles (BRPs).

	Červená Lhota (CL), Great Hall	**Uherčice Castle (UC), Corridor of Angeles**	**Kroměříž Castle (KC), Ground Halls – Terrene salons**
Architectural element	Rib of a cross vault, various fruit shapes	Decoration of a ceiling, flower bud	Garland around a niche, phytomorphic shape
Core mortar (Lp : G : S) vol.	**1 : 0.4–0.5 : 1.8–2.4**	**1 : 0.3 : 0.8**	**1 : 0.3–0.5 : 0.7–1**
CaCO3/CaSO4.2H2O ratio (-)	**0.8–1.6**	**1.2–2.5**	**1.6–2.7**
Lime	High CaO air lime made of marble	Air lime, SiO_2 content around 8 to 10 %wt., made of local marble	High CaO air lime made of limestone
Binder related particles (BRP)	Thermal anhydrite and calcium sulphate dihydrate particles	Lime binder clusters; size < 2 mm No gypsum particles	lime binder clusters, size < 2 mm; gypsum clusters and unprocessed particles, size < 3 mm
Sand	Orthogneiss, quartz, feldspar, dark minerals, mica, angular to roudned; grains < 4 (8) mm	Quartz, feldspars, plagioclases, biotite, phlogopite, chlorites, muscovites, apatite, limestone; angular to rounded; grains < 10 mm	Quartz grains of various colours, gneiss, feldspars (albite), micas (biotite); sharp-angled, sometimes slightly rounded; < 4 mm
Organic additives	Collagen	–	n. d.
Finishing mortar (Lp : G : S) mass	**1 : 0 : 0.5–0.7**	**1 : 0 : 0.7**	**1 : 0 : 0.6**
Lime	Same lime as in the core mortar	High CaO content, low MgO content	Same lime as in the core mortar
Binder related particles (BRP)	Not present	Lime binder clusters; size < 2 mm	Lime binder clusters, limestone structure, size < 1 (2.5) mm
Sand	Similar composition as in the core mortar, grains < 1 mm	quartz and micas, few fragments of silicate rocks; elongated muscovite grains < 1 mm	Similar composition as in the core mortar, grains < 1.5 mm
Organic additives	Collagen	Collagen, casein	n. d.

Table 1. Comparison of stuccoworks, Lp – lime putty (dry content 45%; 1300 kg/m3), G – gypsum powdered hemihydrate (900 kg/m3), S – sand (1600 kg/m3), n.d. – not determined.

3. Considerations for repair of stuccoes

The stucco construction and its attachment to the substrates must be understood as it has vital importance for its preservation. Figures 1 and 2 show an example of repair where the previously transferred stuccoes were fitted back by means of a lime-gypsum mixture, designed based on the original mortar identified through analysis. The characterisation of historic stucco mortar compositions provides valuable information about the mixing proportions, quality of individual compounds used and processes applied to their production that are valuable for their conservation. Understanding subtle differences can lead to further insights into various building phases and distinguishing different craftsmen's teams.

Acknowledgement

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Figure 1. Exposed layers to which the stucco shapes are fixed.

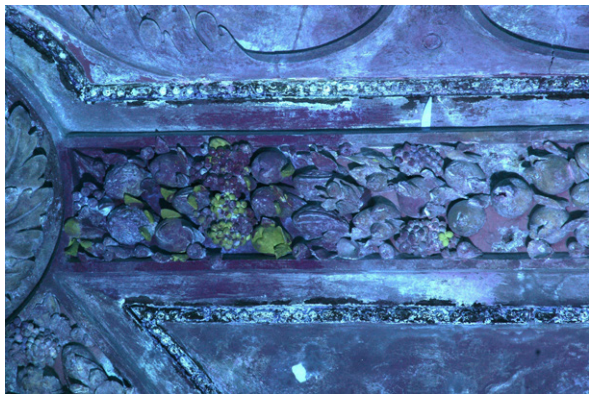

Figure 2. Repaired section, surviving stucco pieces were re-attached, new additions contain ZnO and appear green in UV light.

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Characterisation of Roman Lime Mortars from Red Hall Basilica, Pergamon: Insights into Production Techniques

1. Introduction

The Red Hall Basilica is a Roman Temple in the ancient city of Pergamon, located in Bergama, İzmir, Türkiye. It was built in the 2nd century AD by the order of Emperor Hadrian as a temple dedicated to Egyptian Gods[1]. The Basilica rises on two vaulted tunnels built over the Selinos River and consists of a main building and two towers with domes on either side[2] (Figure 1). It was constructed as a brick masonry and lime mortar, with marble plaques originally coating the walls, where traces of adhesive mortars can still be observed. The Red Hall is a significant and unique structure in Roman Imperial Architecture due to its unconventional design and architectural elements1. Consequently, analysing building material properties of Red Hall Basilica is essential for understanding its significance and construction techniques of its time. In this study, the lime mortars of the Red Hall Basilica were examined to determine material properties and the manufacturing technologies used in Pergamon during the Roman Period.

2. Materials and Methods

Sampling was conducted at different levels and spaces of the Red Hall Basilica (Figure 1). A total of eight lime mortar samples were collected: five containing natural aggregates used in the construction of masonry walls and three with brick aggregates, which were adhesive mortars for the marble covering in the walls (PRM2-3) and on the floor (PRM6). Various analytical techniques were used to characterise lime mortars, focusing on their basic physical properties, raw material composition, chemical and mineralogical composition, microstructure, and hydraulic and pozzolanic properties. RILEM standard test methods were used to determine the basic physical properties. The raw material compositions are defined by the lime/aggregate ratio, which is obtained by dissolving carbonated lime ($CaCO_3$) in dilute hydrochloric acid (5%), followed by washing, drying and sieving of the aggregates. The chemical compositions of the samples were analysed using XRF, whereas their mineralogical compositions were determined via XRD. Microstructural properties were defined by SEM-EDS. Hydraulic properties of mortars were evaluated through TGA by analysing the weight loss between 200-600°C and 600-900°C. Results below 10 indicate the hydraulic properties of the mortars. Pozzolanic properties of aggregates were assessed via conductivity measurements before and after adding fine aggregates (<53 µm) to a saturated $Ca(OH)_2$ solution. Values above 1.2 mS/cm indicate high pozzolanicity.

3. Results and Discussion

The analysis of basic physical properties revealed that the mortars from the Red Hall Basilica have porosity between 18.4–47.6% and density in the range of 1.3–1.9 g/cm³ (Table 1). Notably, the samples containing brick aggregates exhibited the highest porosity (35.8–47.6%) and the lowest density (1.3–1.5 g/

1 Hoffmann 2003.
2 Mania 2015.

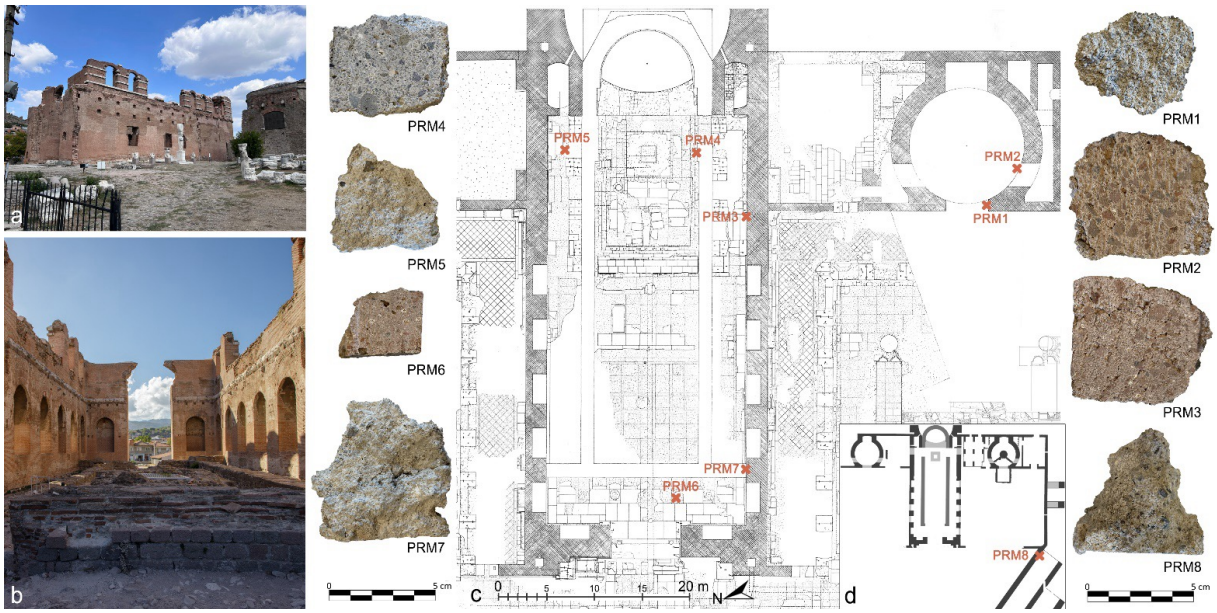

Figure 1. (a) Exterior view of the Red Hall Basilica in Pergamon, (b) Interior view of the Basilica, (c) Architectural plan, and (d) Site plan of the Basilica showing the Selinos River Tunnel beneath the structure, with sample locations marked alongside their photographs.

cm^3), which was attributed to the highly porous nature of the brick material. The average lime/aggregate (L/A) ratio was obtained at 1/3 by weight. The ratio was higher in mortars with brick aggregates. Moreover, the major fraction of aggregates was over 500 µm.

According to further investigations on aggregates, natural aggregates were found abundant in silica (83.7-92.1%), while brick aggregates consist of silica (74.1-86.5%), alumina (5.7-10.0%), and iron (2.0-6.5%) in high percentages (Table 1). Among the natural aggregates, PRM7 differed due to its notably high concentrations of Fe_2O_3, K_2O, and BaO, while PRM8 was distinguished by its elevated SO_3 content, potentially associated with sulphate contamination from prolonged water exposure. Additionally, PRM6, which was used as adhesive mortar on the floor, exhibited a distinct chemical composition compared to the other brick aggregate samples. The main mineral phases detected in the XRD patterns include quartz (SiO_2), albite ($Na(AlSi_3O_8)$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), and K-feldspar ($K(AlSi_3O_8)$), with amorphous substances indicated by a broad diffuse band in the 2θ range of 20–30°. Also, hornblende (Ca2(Mg4Al)(Si7Al)O22(OH)2) was detected in some samples. Electrical conductivity differences of approximately 7.60 mS/cm were measured for the aggregates, indicating high pozzolanic reactivity. SEM analysis revealed that brick aggregates possess a higher porosity compared to natural aggregates.

Lime lumps are small nodules that may form within lime mortars as a result of insufficient slaking or inadequate mixing during their preparation[3]. These nodules represent unreacted remnants of the original lime material. In this context, the lumps sampled from the Red Hall exhibited a high CaO content (96–97%), indicating the use of non-hydraulic lime in the mortar production[4]. The binder was defined as a fine mortar matrix (<63 µm) consisting of carbonated lime and small-grain size aggregates which gave the hydraulic properties and high strength to the mortars[5]. XRD patterns of the binders showed that they were mainly composed of calcite and quartz minerals. The CO_2/H_2O ratio of binders containing brick aggregates ranged between 0.4 and 7.2, while those with natural aggregates ranged between 0.8 and 4.7. Accordingly, all binder samples were classified as hydraulic, as their CO_2/H_2O ratios remained below 10 (Table 1).

3 Bruni et al. 1997.
4 Cowper 1998.
5 Middendorf et al. 2005.

Sample	Aggregate Type	Porosity (%)	Density (g/cm^3)	L/A	Major Oxide Compositions of Aggregates (%)								Trace Element Compositions (ppm)						CO_2 /H_2O
					SiO_2	Al_2O_3	Fe_2O_3	Na_2O	MgO	CaO	K_2O	TiO_2	P_2O_5	SO_3	SrO	ZrO_2	MnO	BaO	
PRM1	Natural	28.11	1.73	0.28	90.48	2.72	2.25	0.21	0.18	0.84	0.70	1.18	8958	2182	217	165	240	352	2.3
PRM2	Brick	35.79	1.47	0.31	74.13	10.01	6.51	0.84	1.14	2.70	2.57	1.16	4476	2012	627	451	657	-	0.4
PRM3	Brick	47.57	1.33	0.46	82.67	6.69	3.88	0.34	0.87	1.36	1.81	1.08	3411	2132	267	308	428	830	7.2
PRM4	Natural	37.10	1.55	0.34	92.11	2.97	1.11	0.34	0.19	0.92	1.17	0.56	1846	954	173	387	-	-	4.2
PRM5	Natural	38.55	1.53	0.37	89.55	3.04	1.48	0.29	0.17	1.02	1.67	1.13	7393	4223	130	710	325	-	3.6
PRM6	Brick	45.03	1.38	0.44	90.00	3.49	1.97	0.29	0.39	1.27	1.06	0.90	1440	1090	253	-	212	-	4.7
PRM7	Natural	27.50	1.64	0.35	83.70	4.93	3.75	0.47	0.21	1.08	2.79	0.92	7480	4730	334	613	402	5410	0.8
PRM8	Natural	18.42	1.92	0.31	86.50	3.15	2.28	0.38	0.15	2.35	1.07	1.06	8130	20700	378	138	-	874	1.2

Table 1. Results of basic physical properties, lime-aggregate and CO_2/H_2O ratios of mortars, and chemical compositions of aggregates.

This suggests that, despite the use of non-hydraulic lime, the hydraulic character of the mortars likely resulted from the presence of pozzolanic aggregates. SEM analysis demonstrated a dense and well-bonded interface between lime and aggregates, with no visible microcracks or irregularities, indicating the pozzolanic and hydraulic behaviour.

4. Conclusion

The basic physical, chemical, mineralogical, microstructural analyses of the Red Hall Basilica mortars containing natural and brick aggregates revealed that their production techniques and material characteristics varied depending on their intended use. Natural aggregates primarily consisted of silica, whereas brick aggregates were enriched in silica, alumina, and iron oxides. The inclusion of brick aggregates also contributed to increased mortar porosity. Despite the use of non-hydraulic lime, the presence of pozzolanic aggregates contributed to the development of hydraulic properties in the mortars. The characteristics of lime mortars of Red Hall Basilica reflect the diverse raw materials and preparation techniques employed in historical construction practices.

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Investigating Sasanian Construction Techniques: a Comparative Study of Mortars, plaster and Stucco at Gawr Tepe (KRI, Iraq)

1. The Archaeological Site of Gawr Tepe (KRI, Iraq) and the MiSAK Activities

Since 2023, the Italian Historical and Archaeological Mission in Kurdistan (MiSAK) of ISMEO and the International Institute of Kurdish Culture in Rome, in collaboration with the Department of Cultural Heritage of Alma Mater Studiorum – University of Bologna and the Directorate of Antiquities and Heritage of Garmian, have been conducting research at the archaeological site of Gawr Tepe (KRI, Iraq)[1].

The site comprises a large settlement inhabited from at least the Sasanian period until the 13th century CE and is characterised by the remains of a monumental palace. While its foundation appears to date back to the Sasanian era, the building was also in use during the early Islamic period.

Despite the site's poor state of preservation—partly due to extensive spoliation and more recent illicit excavations—it has been possible to determine that the Sasanian-period palace featured massive fired-brick structures bound with a gypsum-based mortar. The walls and some floors, particularly those of a large artificial terrace at the centre of which the main building was located, were covered with a thick

Figure 1. The archaeological site of Gawr Tepe (photo MiSAK-Abdul Karim 2023).

1 Colliva, Mancini, Sameen 2023.

layer of white gypsum-based plaster. Additionally, evidence suggests that the palace was richly decorated with stucco during both the Sasanian and early Islamic phases. The mortar and plaster coatings used in the Sasanian-period masonry structures exhibit, according to preliminary optical analysis, interesting similarities in composition to the decorated stuccoes. Unfortunately, no stucco decoration has been found in situ to date, with all recovered fragments coming from secondary deposits.

2. The Comparative and Diachronic Study of Mortars, Plaster and Stucco

The richness and variety of these materials, their potential chronological range, and the opportunity to collect comparative samples from sites that are both geographically and chronologically related convinced us that this was an ideal occasion to initiate a diachronic and comparative study of gypsum-based plastic materials in the region. This initial phase of research has focused on developing an analytical protocol that allows the collection of comparable data from materials that, although differing in function, share the same nature and production techniques. The first analyses have concentrated on samples from Gawr Tepe, but samples from other Sasanian-period sites in the area, including Paikuli and Hawsh-Kurw, as well as Parthian-period sites such as Sarqala, are already being collected or prepared for analysis.
The analyses have been designed and conducted in close collaboration with the Conservation Science Laboratory of the Department of Cultural Heritage at Alma Mater Studiorum – University of Bologna.

2.1 Analytical Techniques for Characterization of Material

The study of the plasters, mortars, and stuccoes from Gawr Tepe employs a multidisciplinary analytical approach integrating different techniques to characterise their composition, production technology, and state of preservation[2]. A preliminary assessment is conducted using stereoscopic optical microscopy, which allows the examination of macroscopic characteristics such as texture, colour, and the presence of inclusions or alteration products, providing valuable information on the overall structure and surface features of the materials and guiding further analyses.
X-ray diffraction (XRD) is employed for mineralogical characterisation, enabling the identification of crystalline phases such as gypsum, anhydrite, quartz, and other associated minerals, which are essential for distinguishing different types of binders and assessing diagenetic alterations over time. The microstructural and petrographic characteristics of the materials are further investigated through thin-section analysis using polarised light microscopy, which facilitates the identification of mineralogical components, textural relationships, and possible technological processes related to the preparation and application of plasters and mortars. Additionally, the sandy aggregate is examined through sample ultrasonic disaggregation to analyse its granulometry and the morphology of clasts, offering insights into the selection and preparation of raw materials—information also useful for conservation and restoration purposes. The characterisation of the aggregates contributes to understanding potential sourcing areas and technological choices in the production of construction materials.

3. Implications and Future Directions

The overarching objective of this research is to deepen our understanding of the technological and chronological aspects of gypsum-based materials in the Sasanian and early Islamic periods. By employing a comparative and diachronic approach, we aim to identify potential regional production traditions, technological exchanges, and material transformations over time. Moreover, particular attention is devoted to assessing the state of preservation of these materials, with the goal of developing appropriate conservation strategies to ensure their long-term preservation and documentation.
This study not only enhances our knowledge of historical building techniques but also provides a foundation for future conservation interventions at Gawr Tepe and related archaeological sites.

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2 Grillini 2018.

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Manufacturing of mortars in Kommos, Crete during the Minoan and Hellenistic periods

1. Introduction

1.1 Location and historical context

The archaeological site of Kommos in Heraklion was established around 1850 BCE. Kommos was the port of Phaistos and a small town with major administrative, industrial, and storage buildings; it was excavated from 1976-1996 by Professors Joseph and Maria Shaw of the University of Toronto[1]. This project included the protection of the ruins, stabilization of the eroded remains and assessment of the performance of ancient mortars. Therefore, at Kommos, 45 samples were collected, with ten selected as representative ones from different historic periods and locations. Mortar samples were studied to assess chronological, structural, decay, and macroscopic characteristics.

1.2 Experimental

The samples were studied macroscopically, followed by a systematic study using microscopic, chemical, and mineralogical techniques. The mortar samples were fractionated and sieved to identify components and binder to aggregate ratios. X-Ray Diffraction analysis was used to characterize the crystalline phases in the mortars. Energy Dispersive X-Rays Fluorescence (EDXRF) and a silicon drift detector was used for qualitative and quantitative analysis of samples. Infrared spectroscopy (FTIR) was used to analyze mortar compounds and salts. Powders from the fine fraction of samples were also used to elucidate binder composition and clay mineral presence. Six samples were embedded in blu-dyed epoxy resin and polished petrographic thin sections were prepared and analyzed in transmitted polarized light in the polarizing microscope. Finally, thin sections were investigated in the scanning electron microscope (SEM-EDS) in order to get more insights into the chemical nature of fine, binder-related components.

2. Results and discussion

2.1 Macroscopical observations and microscopical analyses

The majority of the samples showed a light gray-brown color, especially where lime was mixed with earthen material and sand and all of them were fragile. Based on the macroscopic observations and petrographic investigations two main types of mortar could be identified (Figure 1). The first is characterised by the use of earthen-lime mortars with high amounts of fine aggregates and shell fragments originating probably from local clayey-silty flysch sediments. These mortars also exhibited high micro- and macroporosity. On the contrary, the other type consists of samples of binder-rich lime mortars with the addition of plant fibres as aggregate as well as reinforcement. In these mortars binder-related particles (i.e., lime lumps, carbonate residues, etc.) and different silica grains accidentally burnt with the lime-rich raw material forming secondary calcium-silicate phases, were also detected. Additionally, in the vicinity of some of

1 Shaw 2006.

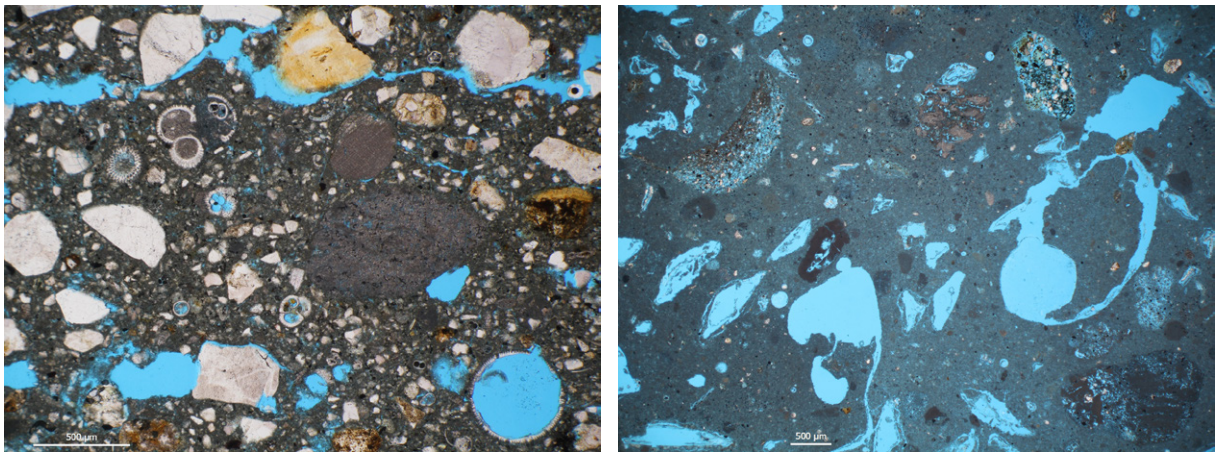

Figure 1. Micrograph of earthen mortars with silica aggregates, fossil shells and a lime lump (left). Fabric of a binder- rich lime mortar with pores after plant fibres and silica-rich binder-related inclusions (right). Plane-polarized light.

these grains hydrate phases could also be observed. Optical microscopy also confirmed in some samples the presence of crushed ceramic fragments and animal hair. A crust due to biological agents was detected on the surface of several samples.

2.2 XRD, FTIR, XRF

The results of X-ray diffraction analysis showed that samples contained silicates (quartz, illite, kaolinite, corrensite, epidote and montmorillonite), carbonates (calcite, dolomite and aragonite) and feldspars (albite, anorthite, and orthoclase) in varying amounts.

The local clay sample analysed was rich in calcite, with clay minerals such as illite, kaolinite, vermiculite, montmorillonite and albite, with high amounts of quartz contrasted with low amounts of dolomite. The XRF analysis of samples revealed that CaO and SiO_2 are the main chemical constituents, the high concentration of SiO_2 and Al_2O3 could be due to aggregate and clay addition, the high MgO content reflects the dolomite presence, and Na2O due to marine slats embedded in samples. The FTIR spectra of the fine fraction of samples, mostly corresponding to the binder, evidenced calcite, aragonite, dolomite, quartz, clay minerals, illite, anorthite, corrensite, kaolinite, vermiculite, montmorillonite, albite, and Al-O bonds.

3. Conclusions

The analysis of mortar samples using optical and scanning electron microscopy, XRD, XRF, and FTIR reveals that they are primarily composed of calcite and/or aluminosilicates (i.e. clay minerals and feldspars), quartz and iron oxide. The differences in composition observed in the mortars are related to chronological differences. The high calcitic nature is attributed to lime as a binder, carbonate aggregates and fossil shells. Silicate components confirm the presence of minerals related to the earthen components and/or aggregates. Consequently, the samples were divided into two groups: lime binder mortars and earthen binder mortars. The earthen mortars were produced using a local clayey-silty sediment mixed with lime to enhance their durability. Microfossils typical for deep-sea suggest the use of a flysch sediment for the earthen part of the binder. The type and grain-size distribution of aggregates suggest that only the coarse grain-size fraction was deliberately by-mixed to the mortar; the finer aggregates were naturally included in the earthen material. To the second group belong very “fat” (i.e., binder rich) mortars with lime character. Aside from binder-related particles, all mortars are free of mineral aggregates; only pores in the shape of plant fibres could be found indicating the use of organic aggregates. Despite the lack of sand, these mortars are practically free of shrinkage cracks, which refers to the good reinforcing property of the fibres. The (partly hydrated) reactions rims around silica grains suggest that siliceous materials were also part of the calcination process and could react in minor extent with the lime to form non-stoichiometric

calcium-silicate phases. These silica-rich residues showed a clear affinity to the mineral phases observed in the earthen mortars. This suggests that the carbonate used for the calcination was related to the geological occurrence from where the earthen material was retrieved (e.g., carbonate rich strata of the flysch sediments, etc.). Finally, the partly poor state of preservation of the (earthen) mortars can be led back on one hand to the high amounts of clayey materials in the mortars and related poor binder capacities, and on the other to the use of partly inadequate cement-bearing conservation materials in the 20th century. Ancient mortars' mineralogical composition and physico-chemical properties ensured long-lasting conservation and provided guidelines for designing compatible and well-performing conservation mortars, preventing irreversible damage to ancient structures .

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Ancient mortars and building materials analysis The case study of the archaeological site of Ville-Marie (Montreal), 1642–1850

Abstract
The Town of Ville-Marie (currently Montreal, Quebec) was created near Hochelaga in 1642 by Paul Chomedey de Maisonneuve and Jeanne Mance.
This paper presents the results of the study of the construction materials used at the time. It appears that while the first constructions were made with lime produced in France, this was later replaced by lime directly produced in Montreal. Traces of lime kilns have also been found.
Different materials (mortars, brick and lime), collected from various structure part of Ville-Marie archaeological sites in Quebec (foundations, walls, paving). Samples were analyzed regarding their microstructural and chemical composition. Scanning electron microscope characterization, X-ray diffraction and Thermogravimetric analysis were performed to assess the sample's composition. The results provided valuable information about the composition of the used materials and the construction history of Ville-Marie between 1642 and 1850.

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Topic 3

Mortars in archaeological sites. Construction history. Archaeometry. Dating of historic mortars

JAN ELSEN, MARINE WOJCIESZAK, LAURENT FONTAINE, ROALD HAYEN, MATHIEU BOUDIN

A protocol for the pre-screening of lime mortars for 14C dating - The importance of optical microscopy

1. Introduction

Radiocarbon dating of lime-based mortars was first developed in the 60's and published by the French researchers Jacques Labeyrie and Georgette Délibrias[1]. They draw already the attention on the need of performing microscopic observations to verify the eventual presence of foraminifers (microfossils) susceptible to false the date results, since they are composed of very ancient carbonates.

Intercomparison among laboratories gives consistent results, whatever the technique used, some samples give reliable results and other samples show a range of dates making them unsuitable for radiocarbon dating using the current common methods available[2,3]. Reference materials such as charcoal or straw extracted from the mortars and dated with 14C or roof frames allowing dendrochronology and contextual information are needed to confirm the 14C dates obtained for a mortar sample. Numerous characterisation methods have been employed to describe the composition of mortars and identify possible contaminants for radiocarbon dating such as thin section petrography and cathodoluminescence microscopy. Petrographic analysis on resin-impregnated thin sections is well suited to determine the mineralogical composition, texture and structure of the binder, and on the different types of carbonates present. It also helps to identify the aggregates, the possible presence of additives, the macroporosity and the state of preservation of the mortar. It is an indispensable first step in the characterisation of historic mortars[4] and has been extensively used for mortar dating studies. Cathodoluminescence by optical microscopy on uncovered thin-sections is used to distinguish the different types of carbonates and it can highlight the presence of other minerals such as quartz, K-feldspar and plagioclase[5]. A bright red to orange/yellow colour is observed for most limestones whereas anthropogenic lime carbonates exhibit a weak, dull tile-red purple to brown luminescence. The colour can vary depending on the instrument used and the limitations of the technique are the lack of luminescence of certain limestones and the limited spatial resolution compared to cathodoluminescence by scanning electron microscopy.

2. Lime mortar components and terminology

Other mortar components, apart of the binder, can have an influence on the radiocarbon content, mainly the ones containing carbonates. These carbonate contaminations are underburnt pieces of the limestone used for lime production, fossil carbonates such as shell fragments or rounded limestone particles naturally occurring in calcareous sands, carbonate-rich aggregates such as crushed limestone/marble/calcite or even crushed (reused) mortars and specific minerals containing carbonates such as layered double hydroxides (LDHs) possibly formed in hydraulic mortars. The presence of geogenic/fossil carbonates re-

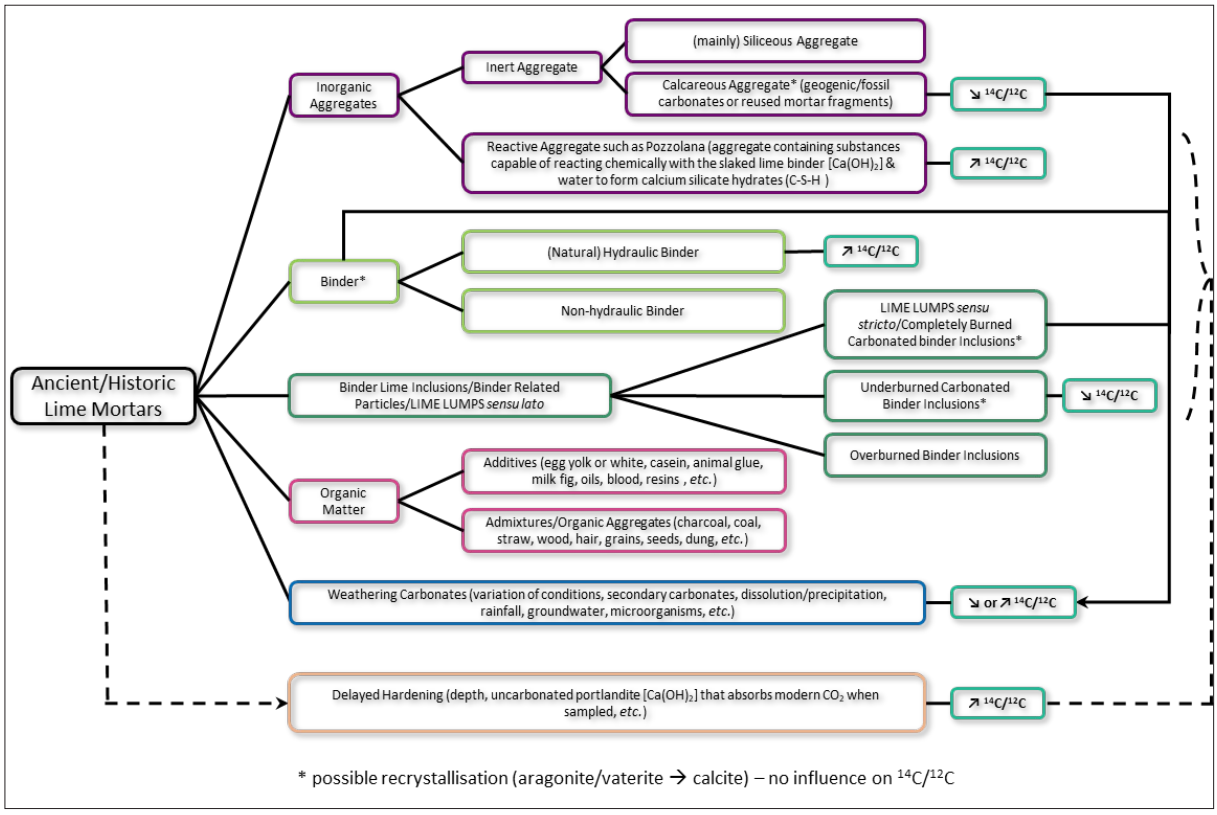
1 Labeyrie, Delibrias 1964, 742.
2 Hajdas et al. 1970, 1845-58.
3 Hayen R. et al. 2017, 1859–71.
4 Elsen 2006, 1416-24.
5 Lindroos et al. 2007, 47-67.

sults in a lower 14C/12C ratio which may generate an older date, as they are radiocarbon free. Another category of carbonates results from weathering and can cause an increase or a decrease of the 14C/12C ratio depending of the incorporation of more recent carbon or older carbon respectively. A final factor to be taken into account is the hardening speed of the mortars. This varies according to different parameters, in particular according to the distance from the surface. Some mortars may take several decades or even hundreds of years to fully carbonate. Figure 1 describes the different mortar constituents with their eventual impact on the 14C/12C ratio.

3. Conclusions

Often, multiple phenomena and/or inclusions can have an influence on the radiocarbon content present in a lime mortar. A careful characterisation is essential to evaluate the possible impact and the reliability of the radiocarbon dating results obtained. Here, we propose to define categories and list the equivalent terms of vocabulary used in the case of mortar radiocarbon dating in order to improve the exchange about concepts and components involved in the process (Figure 1).

It consists of five categories of components (inorganic aggregates, binder, lime lumps sensu lato, organic matter and weathering carbonates) and a phenomenon that can possibly influence the dating of the mortar carbonation (delayed hardening). Some of these categories are subdivided and each subcategory or categories are discussed depending on their possible impact regarding radiocarbon content using acid hydrolysis. Aggregates are classified as inert or reactive, both can influence the radiocarbon content except if the inert aggregates are exempt from calcareous grains. For the binder, the hydraulicity plays a role in the carbonation process and then influences the radiocarbon amount in the mortar. Lime lumps can be completely burned, underburned (which still contain dead carbon) or overburned binder inclusions.



Fig, 1. Mortar constitution and possible influence on radiocarbon dating.

Organic matter might be present in the form of additives, admixtures and microorganisms. Pieces of contemporary and datable organic matter present in the mortar, such as wood, charcoal, straw and hair, should be preferred, if present, for radiocarbon dating lime mortars. When mortars contain weathering carbonates formed by variations of the ambient conditions or by the presence of microorganisms, exogenous carbon may possibly be introduced. On the other hand, recrystallisation into microsparite of the initially micritic texture of the binder and spontaneous transformation of a metastable polymorphs of carbonate should not influence the carbon isotope ratio. Delayed hardening, if present, involves an increase in radiocarbon content and can even results in the introduction of modern carbon when sampling. When using stepwise acid hydrolysis, a statistical analysis of the curve is necessary for improving the estimated date and this will be developed in further studies.

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COUTELAS ARNAUD, HEIJMANS MARC, ROTHÉ MARIE-PIERRE

Petroarchaeological approach of Roman mortars, principles and methods: the case of the city of Arles (France)

1. Context

The scientific community has been interested in ancient mortars and concretes for over twenty years. Roman materials in particular, with their supposedly legendary qualities, are an inexhaustible subject of study. However, historical or archaeological analysis is often sidelined. Instead, the focus is on analytical developments, the identification of raw materials and their origins, or the definition of suitable restoration materials. Our aim is therefore to show examples of archaeological work on ancient lime mortars. This work is part of the discipline of Roman construction archaeology. It is based, on the one hand, on building archaeology and, on the other, on petrography, which we consider to be the fundamental analytical technique for studying these ancient materials. We thus speak of the petroarchaeology of lime mortars.

2. Materials

The city of Arles (Bouches-du-Rhône, France), the ancient Arelate, is at the entrance to the Rhone delta. This town in the province of Narbonnaise became a Roman colony under Caesar in 46 BC. By the end of the 1st century AD, the town already have all the attributes of a large Roman agglomeration: forum, theatre, amphitheatre and thermal baths. A study of the masonry mortars used in public buildings was carried out in early 2000[1]. A total of 79 samples were taken from the crypto-porticoes under the forum, the theatre, the amphitheatre, the circus and the "Esplanade baths".

The recent excavation (2013-2017) of the luxurious Roman houses on the La Verrerie site completes the dossier, thanks to the collection of 58 samples of wall paintings. These relate to both the Harpist house from the 2nd quarter of the 1st century BC[2] and the mosaic domus from the late 2nd and 3rd centuries AD[3].

3. Masonry mortars for public buildings

Aggregates show little variation. The same range of minerals and fragments of siliceous rock from ancient alluvial deposits of the Rhône are always present. These are essentially quartz, with occasional small grain of basalt.

3.1 The Esplanade thermal baths

Excavation of the public baths on the Esplanade site, dating from the 2nd-3rd century AD, has led to the definition of three main architectural ensembles. Analysis of the materials led us to define seven types of mortar[4], one of which (type MS1) was used in all three blocks. Identifying this type of mortar has

1 Coutelas 2003; Coutelas, Heijmans 2006.
2 Boislève, Rothé, Barberan 2020.
3 Rothé et al. 2024.
4 Coutelas, Heijmans 2004.

enabled us to gain a better understanding of the relative chronology of these structures. Other materials are anecdotal, but indicative of various ad hoc arrangements. For example, the coarser MS3 type, with the addition (perhaps unintentional) of various small fragments, such as marble chips or fragments of previous mortars, was used for a wastewater drain.

3.2 Other public buildings

Similar studies were carried out on the other public buildings. It turns out that the MS1 type identified on the Esplanade site also appears to be found in the masonry of the amphitheatre and the crypto-porticoes. It would therefore appear that, if not architectural programmes common to several buildings, at least major public building campaigns took place. These campaigns not only used the same raw materials, but probably also the same teams of masons and the same recipes, which were probably laid down in advance by the authorities.

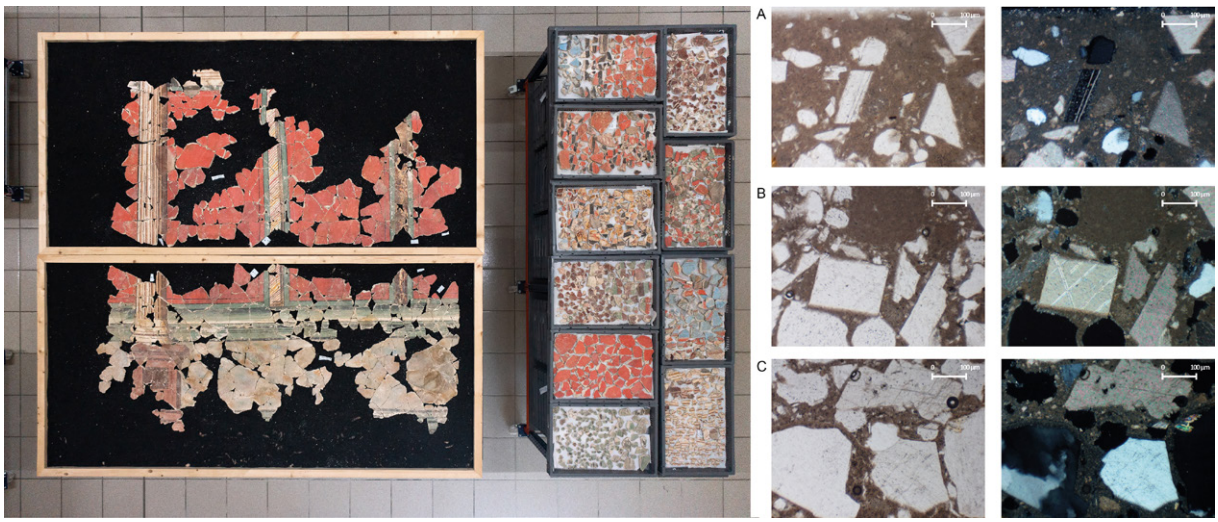

Figure 1. ENS18 painting of the Harpist House on the left (R. Benali, Inrap – MDAA), and microphotographs of the sample in thin section (in plane polarized light on the left side and crossed polarized light on the right). The angular grains visible in A and B are calcite crystals rich in macles. In C the limit between the finishing layer (in the upper half of the image) and the preparation layer, a lime mortar with quartz sand (A. Coutelas).

4. Wall paintings on the Verrerie site

Between 70 and 50 BC, the decorations of the second Pompeian style in the House of the Harpist marked the apogee of the technique, with the systematic use of crushed marble for the finishing layer (fig.1). Some twenty different decorations were used. Although five types of plaster have been identified, analysis shows that they are simply variations on the same technique. These variations are due either to the progress of the project, or to the work of several craftsmen belonging to the same workshop, probably from Italy.

The other period of occupation, from the late 2nd to the 3rd century AD, also provides remarkable information. The technique used to produce the paintings had changed, with limestone crushed in place of crushed marble, a change in practice that was beginning to be seen in other parts of Roman Gaul. Above all, the study reveals several identical renderings for the House with the Tripartite Basin and the House of Aiôn. This suggests that both houses were decorated by the same workshop.

5. Discussion and conclusions

The petroarchaeological approach therefore goes beyond the mere identification of raw materials. On the scale of the city and its public monuments, it shows the existence of major architectural programmes. In

the case of the public Esplanade baths, it has enabled us to gain a better understanding of the construction process. Finally, in a domestic context, an analysis of the wall paintings from the Verrerie site reveals the evolution of mural painting techniques over the centuries, the arrival of Italian craftsmen in the town in the 1st century BC, and the work of the same workshop in decorating two adjoining houses from the late 2nd to the 3rd century AD. So it's not just the materials that are on display, but also the Roman craftsmen themselves.

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Mortar-Like materials on Egyptian Coffins: Investigating the Coffin Set of Nespawershefyt (1000 BCE, Thebes)

1. The issue in Egyptology

Egyptian coffins have been the subject of extensive scientific research, particularly in the study of wood composition and polychrome decoration[1]. However, the mortar-like materials used in their construction have received comparatively little attention. These materials, often composed of gypsum or crushed limestone bound with organic media, sometimes combined with clay minerals and plant fibers, played a crucial role in coffin-making. They were used for structural purposes, gap-filling, decorative substrates, and as a fundamental component of cartonnage—a composite material made from layers of linen, glue, and paste. Analyzing their microstructure and composition provides valuable insights into manufacturing techniques, raw material selection, and broader patterns of technological traditions and craft organization. However, studying these materials presents challenges, as researchers must adopt minimally invasive sampling methods while working with complex mixtures of organic and inorganic components[2]

2. The aim of the project

Building on the pioneering research conducted by the Fitzwilliam Museum team[3], our study aims to develop an analytical protocol to better understand the composition, function, and technological significance of mortar-like materials used in Egyptian coffin construction. Our focus is the coffin set of Nespawershefyt[4], dated to approximately 1070–1000 BCE, which presents a perfect example of the "yellow coffin" typology[5], characteristic of the period, but with a particularly stratigraphy, making it an intriguing case for analysis.

This coffin set features three distinct types of mortar-like materials—mud, pink, and white—each with unique compositions and organic binders, suggesting specialized preparation techniques and specific functions within the overall construction. While preliminary research provided some insights into the white and pink materials—supporting the hypothesis that ground, unheated limestone was used in their preparation—the mud-based material remains largely understudied[6].

Previous studies have often described this layer as minimally processed, sourced directly from the surrounding environment, and applied with added vegetable fibers and occasional calcium sulfate[7]. However, our analysis challenges this assumption, revealing a more complex and deliberate approach to its preparation. This finding not only broadens our understanding of coffin-making techniques but also underscores the sophistication of ancient Egyptian craftsmanship, even in seemingly simple material choices.

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1 Dawson, Rozeik et al. 2010; Amenta and Guichard 2017; Strudwick and Dawson 2019.
2 Rowe, Siddall et al. 2010; Kasso, Stenger et al. 2024; Zaggia, Dawson et al. 2024; Zaggia, Martinón-Torres et al. 2025.
3 Strudwick 2013; Dawson 2016; Strudwick and Dawson 2016; Strudwick, Dawson et al. 2023.
4 Fitzwilliam Museum Accession Number E.1.1822.
5 Niwinski 1988; Taylor 2016; Amenta 2018.
6 Strudwick and Dawson 2016; Brunel-Duverger 2020.
7 Niwinski 1988; Stein and Lacovara 2010; Brunel-Duverger 2020.

Our investigation employs a multidisciplinary approach, integrating optical microscopy, PLM, SEM-EDS, FTIR, and palaeoproteomics to analyze both the inorganic and organic components of these mortar-like materials. This comprehensive analysis has provided critical insights into raw material selection—allowing us to narrow down the likely quarry of origin for the limestone used in these mixtures—as well as the methods of preparation and the broader technological landscape of coffin production during the Third Intermediate Period.

Notably, palaeoproteomic analysis has yielded unexpected insights beyond material composition, offering valuable information on trade networks, species domestication, and even dietary practices—details that remain elusive in traditional zooarchaeological studies.

Through this research, we aim to highlight the untapped potential of mortar-like materials as key indicators of ancient craftsmanship and material culture. Additionally, we emphasize the need for further study of both the organic and inorganic components to achieve a more precise and holistic understanding of the technological skills available in specific regions during this period.

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Ramped Pyrolysis Radiocarbon Dating of Lime Mortars: Method, Application, Advantages, Issues and Future

1. Abstract

Thermal decomposition approaches have been applied to radiocarbon date mortars since the 1960s (Labeyrie and Delibrias), however until recently they have had limited application. In the past few years, there has been renewed interest in thermal methods (Ricci et al. 2020; Toffolo et al. 2020; Daugbjerg et al. 2021) with positive results demonstrated for a ramped pyrolysis technique (Barrett et al. 2021; 2023; 2025). This paper will provide a review of the application of thermal decomposition methods, with a specific focus on the ramped pyrolysis technique. It will describe the underlying theory and principles of the technique as well as the equipment and laboratory methods used. This will include looking at how the difference in thermal decomposition profiles of geological vs anthropogenic carbonates is evident and can be exploited for both screening reliable samples and selecting suitable thermal fractions. The use and limitations of ATR-FTIR as a screening technique will also be explored, notably exploitation of the v2/v4 absorbance bands and their variation based on carbonate component or origin.

Examples of the successful and promising application of the method to a range of materials from across Northern Europe will be presented, including new results from early medieval/medieval Irish and Anglo-Saxon monastic/ecclesiastical structures. These results also include the first encouraging application of the technique to dolomitic mortars. On-going tests on ancient (bronze age) materials from the middle east will also be discussed dependent on the status of measurements.

The above examples will be used to highlight how well the method can work and under which conditions of sample selection this is best achieved. Poorly behaved material and examples will also be presented and used as a platform for discussing the issues associated with sample selection, sample preparation, screening, and ramped pyrolysis application as well as characterizing and validation of what is or is not a reliable result. Finally, future developments and suggestions for improvement of the method will be presented.

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Cocciopesto Through Time: Investigating Roman and Byzantine Mortars in Hierapolis of Phrygia (Turkey)

1. Introduction

Hierapolis of Phrygia (Turkey), located in western Anatolia, was founded in the 3rd century BCE. Despite being repeatedly damaged by earthquakes, it remained inhabited and underwent restoration until the Middle Ages. Many buildings have been restored or even reconstructed, making Hierapolis ideal for archaeological and archaeometric research[1]. This study focuses on the cocciopesto mortars used in public buildings from the Roman to the Byzantine period, offering insights into the minero-petrographic characteristics of the ceramic fragments they contain and into the pozzolanic behavior of these mortars.

2. Materials and methods

To enable a diachronic comparison between the Roman and Byzantine periods, 17 mortars were analyzed: 7 dating from the Roman period (Julio-Claudian to the Severan) and 10 from the Byzantine period (early to the middle Byzantine). A multi-analytical approach was applied to analyze all mortar samples[2]. Polarized light microscopy (PLM) on thin sections was combined with digital image analysis (DIA), X-ray powder diffraction (XRPD), and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). Petrographic analysis, supported by geological knowledge of the Hierapolis area, was crucial for identifying raw material sources and tracing the evolution of mortar composition and ceramic aggregate technologies over time. To better understand the new formed hydraulic phases of these mortars, synchrotron radiation micro-X-ray powder diffraction (SR-μXRPD) was performed on reaction rims between ceramic fragments and binder.

3. Results

All mortar samples contain more than 80 % ceramic fragments as aggregate with a grain size between 100 μm and 1.3 cm and a subangular shape. The remaining aggregate is composed by marble, metasandstone, quartzite, schist, gneiss, phyllite, limestone and ophiolite. In the Roman samples, the ratio between binder and aggregate is between 1:1 and 1:3, while this ratio varies between 1:3 and 1:4 in the Byzantine samples. The clay matrix in the ceramic fragments of the Roman samples has a colour ranging from pale brown to dark brown with a medium to low optical activity, while the Byzantine samples have a pale orange to dark brown colour with a high to very low optical activity. The aplastic inclusions in the ceramic fragments from both historical periods consist mainly of siliceous metamorphic rock fragments (such as metasandstone, quartzite, schist, gneiss), less frequently of marble and limestone fragments. Although the type of aplastic inclusions does not vary, different fabrics are observed in the two periods, which is due to a different content of inclusions, ranging from 5% to 30-40%, and the presence of iso-orientations. The ceramic fragments used in the mortars from Hierapolis belong to locally produced artefacts, as the

1 D'andria 2003; Scardozzi 2015.
2 Pecchioni, Fratini, Cantisani 2020; Cantisani, Fratini, Pecchioni 2022.

aplastic inclusions in the ceramic mixtures are compatible with both the rock outcrops in the Hierapolis area and the Denizli basin. Roman cocciopesto mortars, with ceramic fragments exhibiting a medium to high degree of sintering, remain relatively consistent from the Julio-Claudian period (1st century AD) to the Severan period (3rd century AD) (Figure 1a,b). In contrast Byzantine cocciopesto mortars, show varying degrees of sintering from low to very high, even in the same sample (Figure 1c,d). This may indicate that ceramic production and firing conditions were probably more standardised in the Roman period. The hydraulicity index was calculated using the Boynton formula[3] based on the EDS data of the SEM. These mortars exhibit a hydraulic behaviour that varies from weak to moderate for the two periods. The SR-μXRPD analysis of a selected Roman sample shows the presence of small crystals of tobermorite and hydrocalumite in the reaction rim between the ceramic fragment and the binder.

4. Final remarks

The production techniques of the cocciopesto used in the mortars of Hierapolis of Phrygia evolved over time, while the sources of the raw materials remained largely unchanged. Finally, we observed that in the Roman period cocciopesto mortars were mainly used in water-related buildings such as the Nymphaeum of the Tritons, the Stoa of the Springs and the Great Building (Roman Baths). In the Byzantine period, however, mortars with ceramic aggregates were also used in areas where no hydraulic function was required.

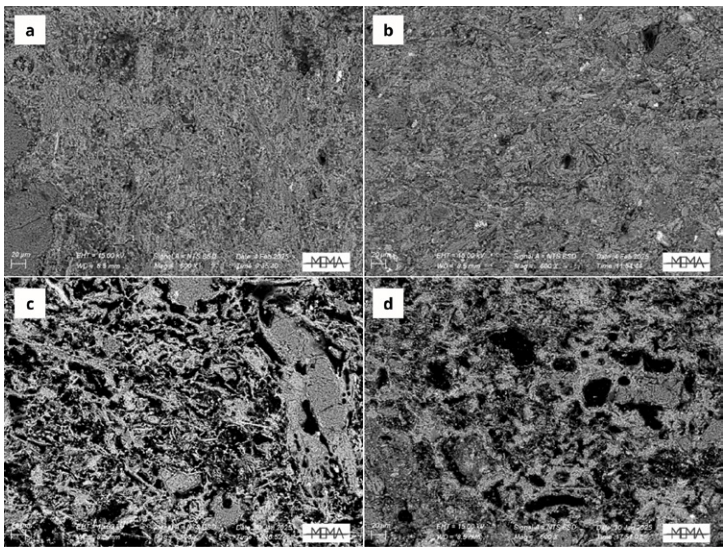

Figure 1. SEM-EDS images obtained at x600 magnification of ceramic fragments in: a) bedding mortar of Theatre (Severan); b) bedding mortar of Thermae (Julio-Claudian); c) bedding mortar of S. Philip church (middle Byzantine); d) grouting mortar of S. Philip church (early Byzantine).

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"Horsing around the pool": Characterization of historic mortars from the Hippodromes Villa in Akaki, Cyprus

1. Introduction

1.1 Description of the excavation site of the Hippodromes Villa and archaeological context.
The Hippodromes Villa is dated in the late Roman period, during the 4th century A.D., and it consists of several architectural structures: reception rooms, a workshop or storage area, a bath complex with two natavio cisterns (swimming pools), a frigidarium (cold bath), a tepidarium (lukewarm bath) and a caldarium (hot bath), latrines, two water cisterns, an aqueduct system for the circulation of water and most notably a large rectangular basin (10 x 14 m), similar to a shallow pool. Another archaeologically important feature of this excavation site is the mosaics which appear in multiple areas of the ancient Villa, with the most impressive mosaic being one with seven panels along a long corridor on the north side of the basin. The central panel, the largest and most important part of this mosaic, depicts a scene of a chariot race that takes place in a circus, hence the name of the excavation site "Hippodromes Villa". It is not yet known if this Villa was a private or public property, but the high quality of mosaic manufacture and attention to detail in the architecture of this building complex, located in the Cypriot countryside away from central areas, offers insights to building techniques developed during the late Roman period in Cyprus[1].

1.2 Research objectives.
The goal of this research was to identify the types of composite materials that were used in this late Roman Villa and examine a possible relation between these materials and the type of architectural structure, the location and chronological period of the site. More specifically, this research aimed at understanding whether the choice of composite materials was intentional, accidental or affected by other factors, such as the availability of local resources and the technology known during the period under study.

2. Experimental methodology

In total, 37 mortar samples were taken from the excavation site in situ. These comprised plasters and mortars with different functions: plasters applied in the large the pool, the water cisterns, the substrate layers of mosaics, the walls from the reception rooms, jointing mortars from the masonries, plasters from all parts of the bath complex and a plaster applied in the roof.
A plethora of archaeometric techniques was applied for the characterisation of the historic mortars. The first step, after sampling, was the recording of macroscopic observations with a hand-held microscope for the identification of multiple layers of material, types of aggregates, and other inclusions. Portable X-ray Fluorescence (pXRF) analysis was performed as a preliminary elemental analysis for the identification of lime, gypsum or lime-gypsum binders. X-ray Diffraction (XRD) analysis was performed to identify the mineralogical composition of the binder and aggregates. Thermal Analysis (DTA-TG) was performed on the binder of the composite materials to identify its composition and determine the

1 Hadjichristofi 2023, 454-465.

hydraulicity of the materials via the inverse hydraulic index[2]. Mercury Immersion Porosimetry (MIP) and water absorption under vacuum were also performed to identify the physical characteristics of the composite materials, such as their open porosity and apparent density, as well as their pore size distribution. Last but not least, optical Microscopy (OM) and Cathodoluminescence (CL) on thin sections were performed to identify in greater detail the nature of the aggregates and binder and the presence of multiple layers.

3. Results and conclusions

The results of this research reveal that at least four types of mortars with different compositions were used in the Hippodromes Villa. The different types of mortars identified relate to the type of architectural structure they were applied on. Type 1 is a pink lime plaster with a high quantity of ceramic powder and fragments; this was applied as first layer in structures relating to water. Type 2 is a white lime plaster with large ophiolitic pebbles that was applied as a substrate layer to the first type of mortars and the mosaics, as well as a wall plaster. Type 3 is a grey lime plaster with a high quantity of small grey pebbles, that was used as jointing mortar in masonry walls. Type 4 is a white gypsum plaster that was used as roof plaster and jointing mortar at the hypocaust masonry of the caldarium. The major mineralogical phases of Types 1-3 were calcite, albite, quartz and actinolite. Type 4 is a pure gypsum mortar. TG analysis revealed that all types, except for Type 4, are hydraulic (Inv. Hydr. Ind<10). Types 1 and 3 with an Inv. Hydr. Ind <5 are distinctively more hydraulic than Type 2 with an Inv. Hydr. Ind between 5 and 8. The porosity of all samples varied between 20-60%. Table 1 shows results for representative samples from each type of mortar identified. The different categories of the mortars used in this late Roman Villa are in accordance with the technology known during the Roman period[3,4]. It is worth noting that, local raw materials, such as aggregates from the Troodos Ophiolitic Complex, and gypsum that appears in abundance in Cyprus[5], were used to produce the mortars under study.

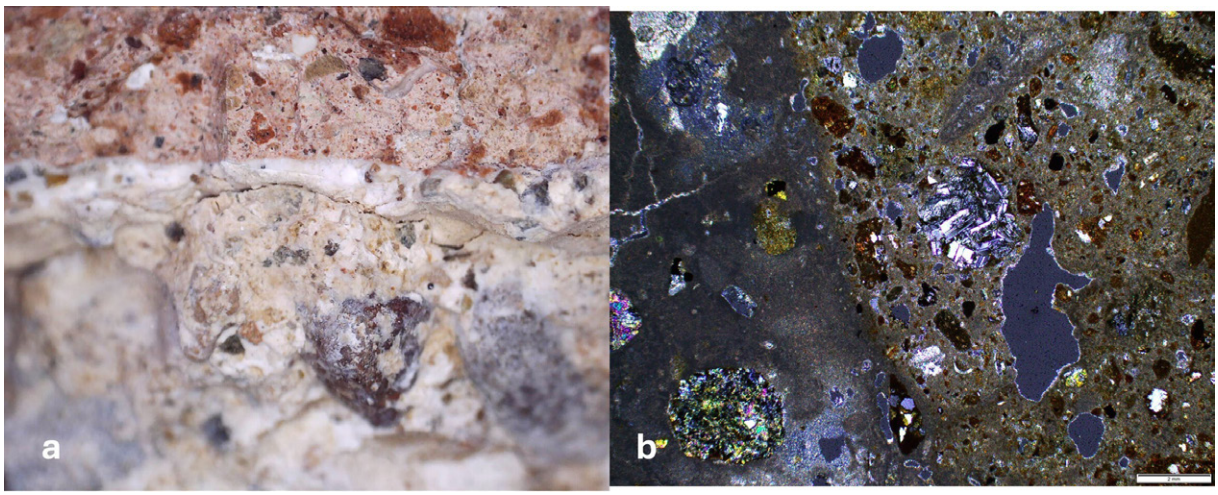

Figure 1. General view of a masonry wall between floor mosaics containing lime mortars in Salar, Granada (left). TEM-EDX mapping of calcite in a replica plaster showing N (blue) concentration from L-aspartic acid at the particle edges as well as in the bulk (right).

2 Moropoulou, Bakolas, Bisbikou 1995.
3 Siddall 2011.
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Radiocarbon dating of mortar: a new system for characterization and laser ablation of anthropogenic carbonate

1. Context

Lime mortar is key to determining the chronology of buildings from Antiquity to the Industrial Revolution, since it is the only type of datable building material that cannot be re-used. The main difficulty in extracting reliable data from lime mortars lies in the presence of components that skew the age obtained by radiocarbon dating. They are mainly of two sorts: geogenic carbonates, which contain only dead carbon and therefore increase the measured age; and secondary calcite crystallisations within the binder, which may induce a rejuvenation of ages linked to the absorption of atmospheric CO2, subsequent to mortar production. These carbon contaminations must be excluded from 14C measurements to avoid false and unreliable dating. Mortar characterization and separation of anthropogenic carbonate are thus necessary and constitute the greatest challenge in direct dating of mortar setting[1-2].

2.New approach for radiocarbon dating of mortar

We present a new procedure for targeted extraction of carbon from anthropogenic carbonate in lime binder based on laser ablation. Unlike traditional protocols, which are applied to a sorted and purified fraction of the powdered mortar, we want to preserve the spatial integrity of the sample in order to more easily locate both the contaminants and the binder.

2.1 Mortar characterization

As a first step, we propose to use low-energy laser-induced breakdown spectroscopy (LIBS) to generate chemical cartographies of the sample surface, enabling the binder to be distinguished from aggregates on the basis of their chemical composition and density[3]. This technique uses short laser pulses focused on the sample surface, vaporizing nanograms of the material and creating a plasma whose light emission is characteristic of its chemical composition. Repeating the process on the whole surface of the sample with µ-LIBS configuration[4] leads to a high-resolution imaging of the sample, providing micrometric precision in binder selection. The resulting data are processed by an artificial neural network (ANN) algorithm to characterize the sample precisely in a fast, automated way, adapted to the large number of data[5]. We combine LIBS-ANN data with photoluminescence and optical microscopy to identify secondary crystallisations, thus creating a mask on the LIBS image to select only the part of the binder likely to produce high-fidelity 14C dating.

1 Hajdas et al. 2017.
2 Hayen et al. 2017.
3 Richiero et al. 2022.
4 Fabre et al. 2018.
5 Herreyre et al. 2023.

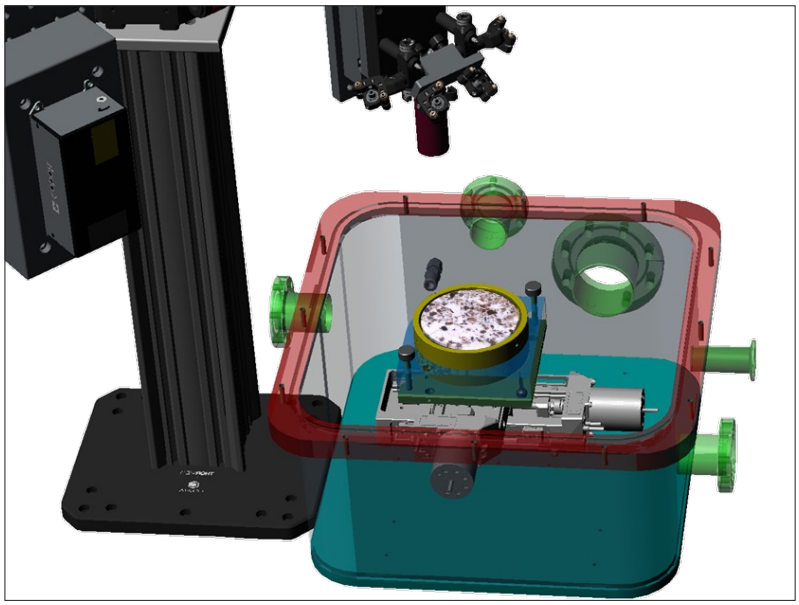

Figure 1. 3D-model of the new optical setup for mortar characterization and carbon ablation.

2.2 Extraction of anthropogenic carbonate from the binder

A second step, the same µ-LIBS instrument is used, not for characterization aims, but for laser ablation, carried out in a controlled atmosphere vacuum, with high energy and only on the areas of interest carefully selected using the previously described protocol. The ablated carbonate material is collected in CO2 form and sent for AMS dating.

We present the use of the new laser ablation system devoted to mortar carbon extraction for 14C dating (Figure 1), with the first results for the method validation. This new approach combining both characterization and dating could be a great tool for archaeologists and building curators.

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NIKIFOROS MEIMAROGLOU, IOANNA NTOUTSI, GEORGIOS MASTROTHEODOROS, ANASTASIA GADOLOU, EROFILI-IRIDIA KOLIA

Characterization of building and decorative materials from the geometric and archaic sanctuary of ancient Helike, Achaia, Greece

1. Introdution – Historical and architectural context

This research employs a range of analytical techniques to study the composition, properties, and production technology of earth mortars, lime-based plasters and painting layers from the ancient sanctuary site of Poseidon Heliconius in the ancient Helike, the famous Achaean city, destroyed by the earthquake of 373 BC (Figure 1)[1]. In 2004, an apsidal temple was revealed, which was erected in the late 8th century BC on the levelling ground of a previous mudbrick altar, according to stratigraphy, examined pottery and other morphological and archeological finds. The load bearing walls of the temple, while presenting differentiations in their construction, mainly consist of rubble masonry of relatively thick joints with fewer ashlar blocks and mostly rounded pebbles in the lower parts, likely sourced from the adjacent Kerynites River, while the interstices are filled with earth mortar. The thickness of the foundations indicates that the temple superstructure was made of mudbricks, although no clear traces of this have been found in the surface layer[2]. An ongoing systematic excavation since 2019, under the auspices of the Greek Ministry of Culture, has provided valuable insights in ancient construction practices of early Greek architecture, in particular regarding one of the least-studied phases, the Early Historical Era and the transition into the Geometric period.

2. Earth mortars

Three mortar samples from different areas of the Temple's walls were examined through soil analysis techniques. All samples exhibit similar properties; they are characterized by a high clay content (28-39.4%), a relatively low sand fraction (29.2-37.2%) and the predominance of very fine sand grains, according to wet sieving. While such high clay fraction content is uncommon in earth construction, the Cation Exchange Capacity (CEC), a key indicator of clay activity related to compressive strength and volumetric shrinkage, was measured at 8.15–11.9 cmol/kg, aligning with the range considered suitable for earth mortars in recent studies[3]. The intrinsic calcium carbonate (CaCO3) content was notably high, ranging among 35% to 41%, a finding that is directly related with the durability of these mortars, as calcite acts as a stabilizing agent of natural soils, particularly against water erosion. Finally, the organic matter content is relatively low, below 2% which is usually the upper threshold for earth construction, indicating that subsoil rather than topsoil was used in the preparation of these mortars.

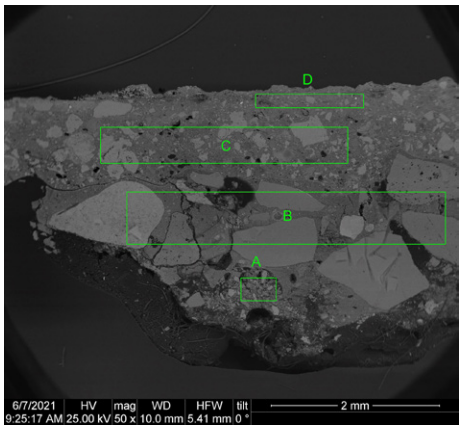
3. Lime plasters and paint layer

Several fragments of plaster showing a rather intense red coating were discovered in various deposition layers; the analysis of corresponding (red-coated) samples revealed a rather complex, four-layer

1 Kolia E. 2011, 106.
2 Gadolou, Kolia 2014, 201-246.
3 Meimaroglou, Mouzakis 2019, 27-39.

Figure 1. Gráfico da densidade e resistividade versus tempo.

plastering system, exhibiting common stratigraphic features but distinct characteristics in material application and microstructure. Microstructural variations of the binding matrix were detected through SEM-EDX (Figure 2a), between different samples in the second layer of the examined fragments; in several samples the binder exhibits large pores and lime lumps, while in others a fine calcitic matrix with elongated pores and the absence of lime lumps are observed. The above suggest differentiations regarding the use and application of lime mortars, and the potential use of quicklime as binder[4]. It is worth noting that the absence of sound interfaces between the upper, pigment-containing layers and their substrate, suggests application of the former layers while their substrate was still damp[5]. Finally, concerning the red pigment used, Raman spectroscopy leads to the identification of mineral hematite (α-Fe2O3) rather than the use of red ochre; indeed, the pertinent spectra show bands at 221vs arising from the symmetric Fe-O stretching vibrations and at 246 (m), 294 (vs), 409 (s), 499 (w, br), 610 (m) arising from the Fe-O symmetric bending vibration (Figure 2b). Moreover, point EDX analysis revealed that the corresponding deep-red pigment grains are composed of almost pure iron oxide corroborating the results of Raman analysis.



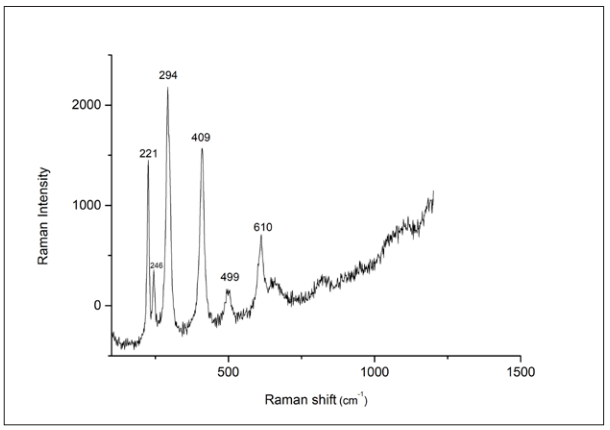


Figure 2. a) SEM image of the 4-layer plastering system; b) Raman spectrum of the paint layer.

4 Karkanas 2007, 775-796.
5 Regazzoni et al. 2016, 333.

4. Conclusions

This research shed light on raw materials, and technological choices behind a range of building and decorative materials; the use of high-quality earth mortars, the different lime application techniques and the potential use of pure mineral hematite suggest a high level of technological adaptation.
While texture analysis, particularly clay fraction, was found to be close to or exceeding the upper threshold suggested in literature, CEC values remained within the recommended range for earth mortars. CEC reflects both clay type and clay content, making it a key factor in determining the properties of earthen materials. Additionally, CEC measurement requires only 5 g of material, compared to 50 g typically needed for texture analysis, making it a valuable tool for the characterization of earthen building materials.

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The Nature of the volcanic materials used for the Construction of the Sebastos Harbor, Caesarea

1. Abstract

The most impressive structure built under King Herod's reign was the artificial harbor of Caesarea Maritima, Sebastos, in honor of the emperor Augustus (sebastos is Greek for Augustus). The structure was constructed on a shoreline devoid of any natural protective embayment, and given such unfavorable geomorphological conditions, innovative building materials and techniques were required to protect it from one of the Mediterranean's highest-energy wave environments. As thoroughly described by the 1st Century CE Roman Jewish historian Josephus Flavius, the construction of Sebastos Harbor "…was to be brought to perfection by materials from other places, and at very great expenses" 1. These foreign materials were incorporated into large concrete blocks of the underwater foundations, described as "…this he effected by letting down vast stones of above fifty feet in length, not less than eighteen in breadth, and nine in depth..." 1, and were recently identified as pumiceous ash and tuff sourced from the Phlegraean Fields volcanic district, Italy.

Pumiceous ash and tuff are found to be the key ingredients in constructing underwater foundations in Roman masonry / construction, as they contain amorphous aluminosilicate compounds capable of reacting with lime and water to precipitate hydraulic insoluble phases with excellent mechanical properties.

This work examines Roman construction and repairs and reports their geochemical, geoarchaeological, and stratigraphic data from on-land Herod palace and underwater wave breakers at Caesarea Maritima Hydraulic mortars. The compositions of immobile trace metals Zr, Ti, and Nb show similar geochemical signals that correspond with the Vesuvian and Phlegraean Fields 2, distinguished from proximal volcanics such as the Kerem Maharal volcano or Golan volcanism. Furthermore, its distinguished from northern Israel Herodian palace at Banias, that resemble the local volcanic sources at the Golan Heights.

Radiocarbon dating of the underwater wave breaker wooden structures show that during the 2nd century CE, Roman concrete was placed, presumably outside of the Herodian layout of the original wave breaker, to facilitate later repairs. The repairs include mortars with evidence for hydraulic reactions based on high-resolution chemical and structural data. In addition, on-land mortars from Herod's Promontory Palace show the presence of pozzolana from the Vesuvian and Phlegraean Fields, suggesting the volcanic materials were used for functions beyond the underwater construction. These observations provide the first archaeological evidence for continuity in importing volcanic ash, i.e., pozzolana, from the area of Naples in Italy, during and after the Herodian construction.

Scholars rely on the writings of Josephus Flavius as the starting point for information about Herod the Great. Recent archaeological excavations in Caesarea Maritima allowed material scientists, archaeologists, and geochemists to find the links between historical texts and Roman concrete in the Sebastos Harbor.

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Challenges in 14C dating of Florentine historic mortars

1. Introduction

Florentine historic mortars consist of a natural hydraulic lime binder obtained by burning a marly limestone, locally known as Pietra Alberese (Monte Morello Formation), mixed with silicate and carbonate sand[1] . This study evaluates the feasibility of applying the 14C dating method to binder rich fractions or lumps to determine the construction phases of religious and historic buildings in Florence and its surroundings. A multi step procedure was implemented to select datable fractions in mortars[2].

2. Materials & Methods

A selection of mortars from significant Florentine religious and historic buildings was analyzed, including San Giovanni Baptistery (17 core samples), Santa Felicita Church (10 mortar samples), Medici Riccardi Palace (6 core samples), Trebbio Castle (27 mortar samples). The sampling strategy was based on well-defined research questions related to chronology, combining historical documentation with analysis of the masonry (Step I).

A comprehensive petrographic and chemical characterization of the mortars was performed using optical and electron microscopy (OM, SEM-EDS), X-ray diffraction on powders (XRPD), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) (Step II). If a mortar exhibited datable characteristics, a mechanical separation of binder-rich bulk and lump was conducted, starting with selection under stereomicroscope. Step III involved a non destructive approach designed to prevent contamination from geogenic calcite. This was achieved by combining XRPD, OM-CL with ATR-FTIR and micro-Raman spectroscopies to determine the calcite origin in the powder samples selected for dating. Different types of calcite interact with electromagnetic radiation based on their atomic and molecular arrangement. FTIR and Raman spectroscopies were used to identify short-range order at the molecular level.

In ATR-FTIR mode, two trend lines were created based on the peak heights of v2 and v4, distinguishing between geogenic and anthropogenic calcite[3]. In micro-Raman spectroscopy, anthropogenic calcite samples displayed a shift to lower wavenumbers in the L, v1 and v4 bands, as well as broadening of the full-width at half maximum (FWHM) of these bands compared to geogenic calcite. Machine learning was employed to predict the origin of unknown calcite[4].

These non-destructive techniques allowed for the preservation of sample mass, ensuring that the same sample could undergo identical analytical procedures and treated for 14C analysis.

In Step IV, the so-called Lilliput graphitization line at the LABEC INFN laboratory in Florence was integrated with a reaction chamber specifically designed for the extraction of CO2 from carbonates .The Lilliput line can process samples as small as only 50 µg of carbon, far below the “traditional” sample size

1 Cantisani et al. 2021.
2 Calandra et al. 2024.
3 Calandra et al. 2022.
4 Toffolo et al. 2023.

of approximately 700 µg[5-6]. This capability allowed the feasibility of dating even individual binder lumps in mortar samples. Typical processing masses for mortar samples were:—approx. 2.5 mg in the case of lump; —approx. 5 mg in the case of bulk mortar.

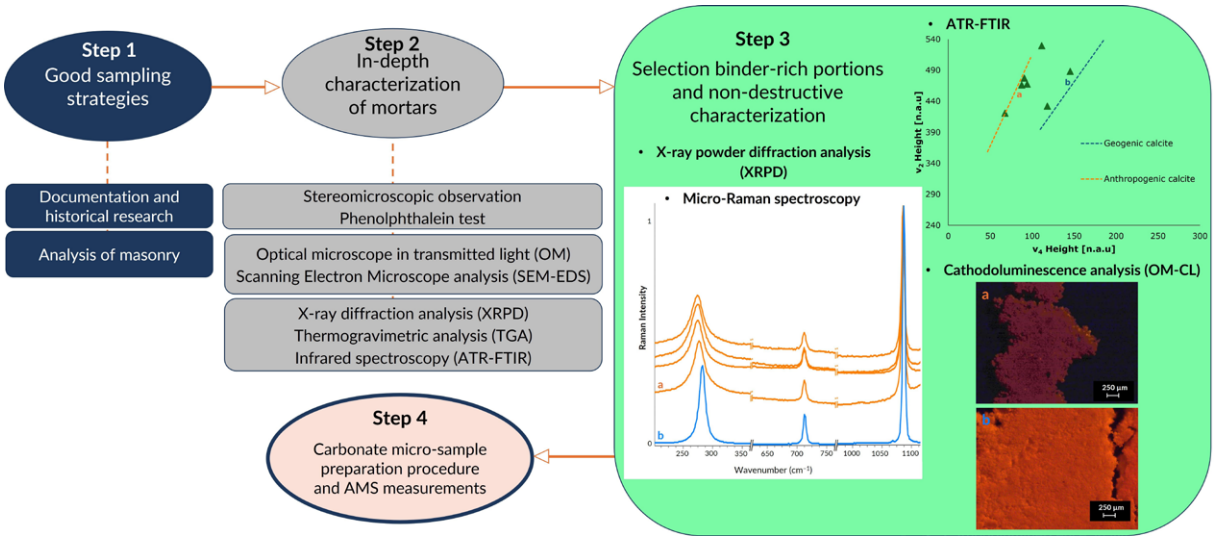

Figure 1. Graphical representation of our multi-analytical procedure for radiocarbon dating of historic mortars.

3. Results and final remarks

The applied procedure enabled the selection of suitable mortars for dating, even in the case of natural hydraulic binder based mortar, a type of mortar that is not entirely aerial and would otherwise have been excluded.

The complete characterization of the Florentine natural hydraulic mortars, performed in Step II, allowed for the selection of the most appropriate mortar fractions for dating with the 14C method: the binder-rich portions from Trebbio Castle, as well as those from the Church of S. Felicita and the Medici Riccardi Palace were identified as optimal candidates. In contrast, the characteristics of the mortar samples from the Baptistery of S. Giovanni did not allow the selection of datable material, due to high content of fine carbonate aggregates, the presence of stone remains from lime production as well as the limited binder fraction and recrystallization phenomena. XRPD, ATR-FTIR, OM-CL and micro-Raman analyses effectively identified powders composed mainly of anthropogenic calcite, excluding contamination from geogenic calcite. The most innovative aspect of the overall procedure is that the exact same material characterized is subsequently used for radiocarbon dating.The obtained results align with the expected chronological ranges, demonstrating that the overall analysis was essential for selecting material free of geogenic contamination. The use of non-destructive methods proved crucial in multi-analytical studies of unique and small samples.

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Study of the provenance of raw materials for the mortars from the Mikulčice archaeological site, Czech Republic

1. Introduction

Mikulčice (South Moravia region, Czech Republic) is an important archaeological site and one of the oldest fortified Slavic settlements in Central Europe. The age of this site is related to the 9th century. Of considerable importance are the preserved masonry buildings, which are also one of the oldest lime and stone masonry remains in the Czech Republic. Although the site has been studied extensively, the provenance of building materials is still not clearly understood.

A number of historic mortar samples from the site were collected in order to study their composition and structural characteristics. The aim of this study was not only the characterisation of the historical mortars, but mainly the evaluation of the potential sources of raw materials. In addition to the historical mortar samples, a set of carbonate rocks was collected, characterised and evaluated.

The archaeological complex referred to as the Mikulčice-Kopčany settlement agglomeration is divided into two parts. The castle (fortified core) was situated on the right bank of the Morava River in the Czech Republic[1]. The extra mural settlement and the hinterland of the centre were situated on both banks. On the left bank, in Slovakia, close to Kopčany village, still stands the pre-Romanesque Church of St. Margaret.

2. Materials and methods

The historical mortars from the Mikulčice archaeological site were sampled from the excavation trenches, mostly from the church relics. Some of these samples were selected for characterization in order to study the quality of the lime binder and to determine the properties that could lead to the discovery of the original raw material for lime production[2].

Sites for sampling of raw materials were selected on the basis of a literature search, geological mapping and the current availability of resources that could potentially be used for the construction in the 9th century.

33 samples from archaeological probes and relicts of historic masonry were characterised by several analytical techniques. Polarized light microscopy (PLM), scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) or and cathode luminescence (CL) were used to determine petrographic characteristic and mineralogical composition. Thermal analyses (TA) and quantitative X-ray diffraction (XRD-QPA) were used to determine the chemical and mineralogical composition and hydraulic properties of the studied mortars. Very important was the stable isotope analyses (δ13C and δ18O) of carbonate unburnt or underburnt particles. These results could then be compared with potential raw materials.

24 samples of limestone raw materials were analysed by polarized light microscopy (PLM), and cathode luminescence (CL). The stable isotope analyses (δ13C and δ18O) results were essential for comparison with the lime particles in historic mortars.

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1 Poláček 2018.

2 Kozlovcev et al. 2022.

3. Results and discussion

In studied mortar samples, quartz grains represented the predominant filler component. Less frequent were feldspars (sodium and potassium), elongated mica, apatite grains and small opaque minerals. The binder consisted of a fine-grained carbonate matrix. The structure of the binder was uniform, without any significant transformation or traces of degradation. Binder related particles (BRP) frequently occurred in the studied samples. These particles were of interest because some of them reflected the original raw material - frequent unburnt limestone fragments (Figure 1 A, B), while the others were in the form of lime lumps sensu stricto[3]. Unburnt fragments were classified as a micritic limestone and contained sparite rich zones and bioclasts[4].

Due to the location of the archaeological site in the six-kilometre-wide floodplain of the Morava River, there are no sources of solid building stones in the immediate vicinity. The building stone material was obtained from two sources on the Slovak side at a distance of 6-18 km from the fortified center. Especially from the vicinity of Holíč come various young limestones (sandy, lumachel, oolitic) of Sarmatian age, around 12 million years old[5]. The second source of building stone were calcareous sandstones of the older Tertiary Palaeocene, 66-56 million years old[6]. They are part of the White Carpathian unit of the flysch zone and their first surface occurrence is eastern of Holíč or near Skalica.

The surroundings of Holíč, Skalica and Sudoměřice were explored in order to find possible sources that could have been historically used for lime burning. However, the problem was the searching of for materials used more than 1000 years ago. The whole landscape and environment have undergone major changes.

Comparison of the stable isotope results of unfired fragments from historic mortars and samples of collected raw materials resulted in only partial agreement. This may have been due to the unavailability of the raw material corresponding to the mortar materials or to the partial changes in isotopic composition caused by the high burning temperatures, although samples without obvious thermal damage were primarily analysed.

Based on microscopic analysis, the raw materials from the Sudoměřice stream bed (fine-grained micritic flysch limestone) were most consistent with limestone fragments from historical mortars (Figure 1. C).

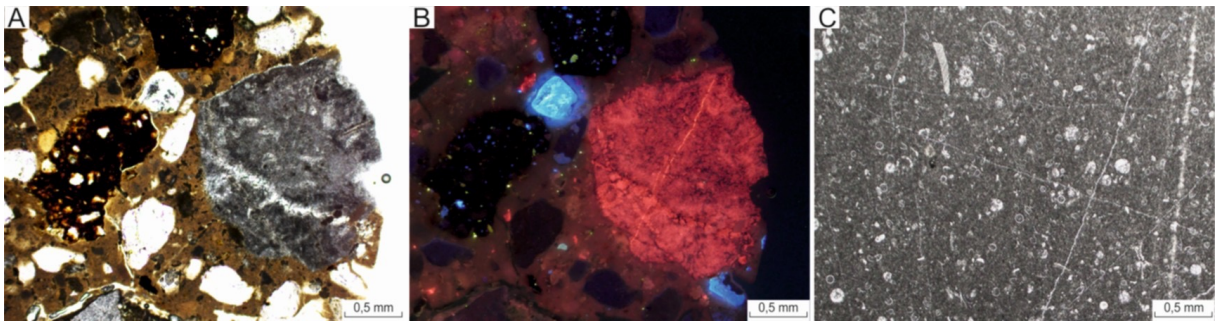

Figure 1. A: historical mortar of Mikulčice, sample ML 29 (PLM). B: bright red/orange luminescence of limestone fragment, sample ML 29 (CL). C: fine-grained microstructure of limestone sample from Sudoměřice stream, sample VSUD 2 (PLM).

4. Conclusion

The study focused on research of archaeological samples from the Mikulčice site. After material analysis, raw materials that could have been potentially used in the past as building materials were examined in re-

3 Elsen 2006.
4 Dunham 1962.
5 Vass 2002.
6 Waśkowska et al. 2014.

lation to the numerous unburnt limestone fragments in the mortar samples. The survey showed that the limestones from Sudoměřice streem were most consistent with unburned fragments in mortar samples.

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How Ancient Mortars Tell the Story: A Large-Scale Research Approach to Medieval Castles

1. Introduction PRIN 2020 CASTLES Project

The PRIN 2020 CASTLES Project focuses on studying mediaeval castles in Italy, particularly their chronology and transformations through archaeometric analysis of mortars and charcoal. The project is based on a multidisciplinary approach and aims at establishing a new chronology for the construction sites of incastellamento (11th-12th centuries), focusing on the timings of castle development. Defining an accurate chronology is crucial to understand the historical, archaeological, and economic context of these buildings. Between the mid-11th and late 12th centuries, fortifications shifted from predominantly wooden structures to stone and mortar settlements, often consisting of towers, churches, village buildings, and defensive walls. To examine this transition, a multidisciplinary team integrated their expertise to explore the subject from multiple perspectives. The team consists of archaeologists and historians (Units 1 and 2, respectively the Universities of Siena and Turin), geologists and conservation scientists (Unit 3, University of Florence), and physicists and archaeologists (Unit 4, University of Campania "Luigi Vanvitelli"). The group selected several sites across three regions of Italy (Piedmont, Liguria and Tuscany) for the study, before applying the multi-analytical method shown in Figure 1a to each site. The criteria for selecting the castles are shown in Figure 1b.

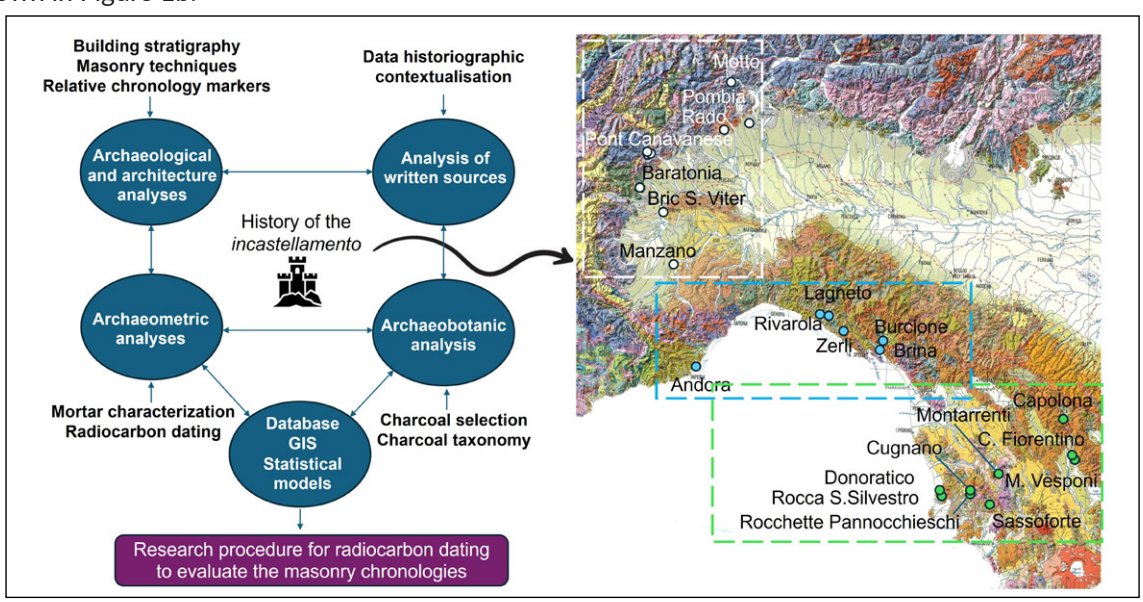

Figure 1. Integrated research workflow combining archaeological, archaeometric, archaeobotanical, and historical analyses for the study of castles (a). Main criteria for the selection of castles (b). Geographical distribution of the selected case studies in north-central Italy (Piedmont, Liguria, and Tuscany) (c).

2.Archaeometric research

Radiocarbon dating (14C) is one of the most widely used absolute dating techniques in the field of archaeology and Cultural Heritage. The use of the 14C method for dating ancient mortars was proposed as early as the 1960s, applying the method to the inorganic material (binder calcite). In mortars, the inorganic radiocarbon-datable component is calcite, which is formed by the reaction of calcium hydroxide with atmospheric CO2 during the setting of the material (the so-called anthropogenic calcite). Aerial mortars are the most suitable for dating, because they set and harden completely, incorporating atmospheric CO2. Moreover, the mortar mixture can include charred wood inclusions, corresponding to potential residues of the fuel used in the limestone calcination process (so-called charcoal). Since mortars are complex and heterogeneous materials, other sources of C can be present in the mortar samples, which may contaminate the 14C concentration[1]. Therefore, selection of the datable fraction and elimination of potential contamination proves to be a challenge for the international radiocarbon community. We combined 14C dating of mortar and charcoal samples to evaluate masonry chronologies.

The project aim is to propose effective mortar characterisation procedures (including mortar sampling and characterization) to choose samples suitable for dating. Therefore, a detailed minero-petrographic, chemical, and physical characterization (XRPD, PLM, phenolphthalein test, SEM-EDS, OM-CL, ATR-FTIR and penetrometric test) was carried out to extract the binder and lump samples suitable for dating[2-3]. Only the samples with suitable characteristics were treated with the CRYO2SONIC preparation method, and accelerator mass spectrometry (AMS) measurement, for the evaluation of the radiocarbon content[4] . Samples were pretreated at the iCONa Lab of the University of Campania and radiocarbon dating was performed at the Centre for Isotopic Research for Cultural and Environmental Heritage (CIRCE) laboratory (Caserta, Italy).

3. Preliminary results

This multidisciplinary research focused on a series of 25 carefully selected castles (Figure 1c). The selection of investigation sites was determined by the archaeological analysis of the architectures and by examination of historical data. The historical and archaeological study of these sites facilitated the selection of specific locations for mortar sampling. To overcome the complications of radiocarbon dating mortar (e.g. issues linked to water-sheltered masonry), effective sampling strategies and analytical procedures for mortar characterization were implemented.

The innovative aspect of this project lies in its multidisciplinary methodology and in the in-depth analysis of 120 samples from a broad geographical area.

The minero-petrographic and chemical data allowed characterizing the raw materials of each sample, and above all highlighting suitable mortars for dating, meaning those constituted by air hardening calcic limes, weakly hydraulic lime, and weakly hydraulic lime with a magnesian component with presence of anthropogenic calcite in sufficient amount.

The mortar radiocarbon dating indicates a time span between the 11th and 14th centuries. These results were also compared with the radiocarbon concentrations of charcoal. From preliminary data, several chronologies can be developed for the individual site or for a broader phase of incastellamento.

This large and diverse sample set provides a rare opportunity to examine the different production techniques and materials used in different regions, which are often crucial for dating. Despite the challenges involved, the successful establishment of the chronology of numerous mortars has provided significant scientific, historical and archeological insights and contributed to a more accurate understanding of political, social and economic processes connected with the construction and transformation of medieval castles in Italy.

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1 Hayen et al. 2017.
2 Pecchioni et al. 2020.
3 Calandra et al. 2024.
4 Ricci et al. 2019.

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Archaeometric investigations on mortars used in rural settlements in the Piedmont Po Valley (Northern Italy) through comparisons of the Mg/Ca ratio in the limestone quarries used for the supply

1. Introduction

The Po Valley in Piedmont has numerous rural settlements characterised by a wide range of structures dating back to the early Imperial Roman period and the Late Medieval period, which were erected and partly modified in different historical phases. This rural architecture is of great heritage value, as it contributes to a deeper knowledge of the historical development of Piedmont. In particular, this work analysed lime, one of the oldest and most important building materials, used in the bedding mortars of three archaeological sites of rural buildings in the Monferrato area of Piedmont. Mortar is often the only structural element that is certainly coeval with each construction phase of the buildings and therefore it was considered useful to attempt to characterise it initially as a diagnostic element between phase and phase of each site and then as part of a broader examination of the variation in the exploitation of resources (carbonate rock quarries) between the different phases and the identification of possible causes. Several works have focused on the study and mineral, petrographic and chemical characterisation of ancient mortars in order to investigate the technological and supply areas[1]. An efficient, rapid and low-cost geochemical diagnostic method based on the characterisation of two oxides, MgO and CaO, in the lime of the mortars and in the carbonate rocks of the area is presented. The variation of this ratio has proven to be useful for the relative dating of building walls and for identifying geological formations and quarries that may have been used during different architectural phases.

2. Materials and methods

Mortars consist of a mixture of an inert material (usually sand), a binder (lime) and water. Lime, obtained from the firing of carbonate rocks (limestone, dolomitic limestone, dolomite...), is one of the most common building materials in the world and has been used since ancient times. In this study, the contents of two chemical elements, Ca and Mg, were analysed in the mortar samples taken from the structures of three rural settlements, Brusasco, Trino and Ticineto, of Roman and medieval origin[2-3] located in the lowland area along the alluvial strip of the river Po. The same analysis was conducted on rock samples taken from ancient limestone quarries in the nearby hilly area of Monferrato.

Rock sampling was preceded by a survey of the area, paying particular attention to the routes of ancient roads and areas showing traces of past excavation activities that could be attributed to ancient quarries.

1 Gambino et al. 2022, 23.
2 Negro Ponzi Mancini M.M. 1980.
3 Negro Ponzi Mancini M.M. 1999.

3. Results

To distinguish different types of lime, the ratio of Ca and Mg has proven to be a valid method. These two elements are constantly present in both the limestone samples and the binders used in wall and building mortars.

Calculating the ratio of the two elements (Mg/Ca) and comparing the values obtained from the mortar and rock samples was useful for characterising and differentiating the limes and limestones used for lime production and for obtaining information on the potential sites for lime supply and their changes over time. The analyses show a wide range of MgO/CaO ratios in all rock samples (ratios ranging from 7x10-3 to 303x10-3). However, in almost all cases, the MgO/CaO ratios of the rock samples analysed show values typical of quarries in the same geological formations. In general, the quarries used for lime production come from the same geological formation, which result in a relatively uniform chemical composition of the limestone. Furthermore, the analyses show that the MgO/CaO ratio allows the samples to be divided into classes corresponding to the different origins of the limestone.

The MgO/CaO ratio has been shown to vary in the different archaeological phases, but not to be very variable in the same group of buildings; in particular, the MgO/CaO ratio in the mortars is between 7x10-3 and 35x10-3 in Brusasco, between 50x10-3 and 150x10-3 in Ticineto, while it is very variable in the rural buildings in Trino.

4. Conclusion

The correlation between the Mg/Ca ratio of rock samples from the limestone quarries in the area and the archaeological stratigraphy confirms the use of limestones of different origins at all sites in different chronological phases (Roman and Medieval).

The comparative analysis of the MgO/CaO ratio in rock and mortar samples, combined with the archaeostratigraphic and local context analysis of historical infrastructures, has proved to be a useful tool for the spatial correlation between different sites and the temporal correlation with respect to the extraction phases.

In this context, mortar has proved to be an important diagnostic tool to identify the original limestone quarries and the period of exploitation, and to provide interesting information on the network of trade routes and their changes over time. The provenance of limestone can therefore provide interesting information about the network of trade routes and their changes over time (Figure 1).

In fact, it has been observed that quarries exploited in an earlier period (e.g. Roman times) were often no longer exploited in more recent periods (e.g. medieval or late medieval times). The reasons may not only be related to the impossibility of quarrying or need of different characteristics of limstones, but also to political and road changes.

The characterisation of ancient mortars and the comparison and correlation with their sources of supply are certainly the starting point for opening up new, innovative and multidisciplinary lines of research on geomaterials in the field of Cultural Heritage.

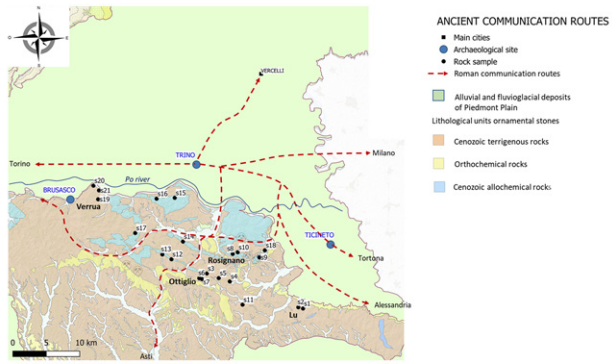

Figure 1. The most important Roman and Medieval settlements and the main communication routes built in Roman times

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PETRA URBANOVÁ

Luminescence dating of mortars through single grain procedure at European scale: potential and drawbacks

Luminescence dating techniques are widely used in geology and prehistoric archaeology since the 70s', but its first applications on mortar dating started to be explored only at the beginning of the new millennium (Goedicke 2003). Since then, a considerable methodological progress has been made in the field (Urbanová et al. 2020). As a result, luminescence dating of mortars through single grain technique (SG-OSL) is nowadays recognized as a reliable research method that has been employed in various archaeological research projects across Western Mediterranean. Among the most recent ones, we may name Monacorale project on Croatian Heritage 2021-2025 (running, Čaušević-Bully et al. 2018), ArchiDate project on Italian sites funded by the University of Padova and LaBEx Bordeaux Archaeological Sciences 2019-2021 (Urbanová et al. 2022), MEMOAr project funded by French National Research Agency 2022-2025 (running) or MoDAq project 2016-2019 funded by Region of French Aquitania (Javel et al. 2020, Urbanová et al. 2023), both studying various monuments of the French territory. The large scope of geological contexts in which the SG-OSL dating of mortars has been employed in the last 15 years allowed mapping its potential but also better understanding its limits. The paper aims to discuss these questions from the overall (European) perspective.
The basic premise for luminescence dating of mortars is that the quartz extracted from archeological sample was set to zero by light – bleached – at the moment of mortar making. If it is the case, the archeological dose absorbed by mortar since its fabrication is proportional to its age. In reality, although some mortars can appear perfectly bleached, a majority of them contains a mixture of grains with different degrees of bleaching which made the application of luminescence dating on mortars problematic in its beginnings. A fundamental turn has been achieved around 2010 thanks to the expansion of the "single grain" system developed at the end of the nineties' (Duller 1999). The latter - contrary to the standard "multigrain" procedure - allows measuring luminescence signals of individual grains instead of measuring an average luminescence arising from hundreds or thousands of grains. The difficulty to date partially bleached mortars has thus been overcome.
As the methodology was applied on quartz extracts from different geological contexts across Europe, it allowed showing differences in quartz sensitivity which is highly variable and difficult to predict. In luminescence dating of mortars, only a very little proportion of analyzed grains gives a detectable signal. In some cases, it can be up to 5 %, while in many other cases it can be less than 1 % or even less than 0.5 %. At some point, the proportion of luminescent grains becomes so low that we have to ask about the feasibility of dating.
There are relatively few research studies that explore a relationship between quartz sensitivity, its geological origin and its sedimentary history. While some specific cases suggest that geological province and sediment source have major influence on quartz luminescence sensitivity (Sawakuchi et al. 2011, Capaldi et al. 2022), other cases propose that sedimentary history of the quartz plays a predominant role in the sensitization of quartz (Pietsch, Olley, Nanson 2008). It further demonstrates the complexity of the subject. The recent Guide for interpreting and reporting luminescence dating results (Mahan et al. 2022) suggests that regions sourcing quartz grains with high-luminescence sensitivity usually have slow erosion rates, long transport distances and are preferably sourced from sedimentary bedrock. On the contrary, areas of active orogens with rapid bedrock erosion and volcanic activity are locations that have been

noted as containing quartz with low sensitivity. Although more detailed research needs to be undertaken, current observations on quartz sensitivity extracted from mortars across Western Europe seem to match with some of these findings. For example, quartz extracted from mortars in coastal Mediterranean areas shows good characteristics for SG-OSL dating. On the contrary, the same mineral originating from mortars sampled close to Switzerland Alps does not emit any detectable signal. But publishing unsuccessful dating studies is less rewarding, and such results remain often unpublished or do not raise much interest. In order to avoid extensive sampling campaigns in the cases were the chances to get conclusive dating results are low, the goal of this paper is to put the collected data on quartz sensitivity collected on about 40 historical sites in Croatia, Italy, France and Spain in context and to make non-specialists aware of this particular issue.

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Characterization and 14C Dating of Early Medieval painted stucco mortars from St Martin church in Disentis (Switzerland)

1. Introduction

Excavations at Disentis Monastery, situated in the region of Grisons, Switzerland, at a strategically important crossroads to the Lukmanier Pass, have yielded a remarkable number of painted stucco fragments that provide valuable insights into the history of Carolingian art and culture. These fragments, discovered as early as 1908 and later during comprehensive excavations in the years 1934 and 1980-1983, are a testament to the site's historical significance. The analyses of the current research focus on a selection of fragments from the large number of excavated plaster fragments, with the aim of contextualizing them within the overall architectural system.

What we know so far attests to the existence of three cult buildings from the 8th century onwards. In the will of the Chur bishop Tello of 765, the existence of three places of worship side by side, respectively (from north to south) dedicated to St Mary, St Peter and St Martin, is recorded. The church of St Martin was probably erected in the first half of the 8th century. Around 800 CE (Common Era), a new renovation phase affected St. Martin's and led to the construction of a hall building with a three-apse end. Most of the approximately 12.000 stucco and plaster fragments recovered during excavations were found in demolition layers belonging to the destruction of the first church of St. Martin, built around 700 and replaced by the triple-apsed church around 800. These two dates represent the lower and upper boundaries for the dating of the stucco decoration.

Since the stucco decoration has been recovered from archaeological layers deposited after the destruction of the first church, there are some uncertainties in their chronology. Another issue concerns whether there are differences in composition between various group of fragments, which could indicate the presence of different decorative phases. To answer these questions, petrographic examinations and 14C analyses have been carried out on a selection of samples.

2. Materials and methods

The selected samples and their description are reported in Table 1.

Petrographic analysis was carried out using a polarizing light microscope (PLM) Zeiss Axioskop 5 equipped with a digital camera Axiocam for capturing images with a resolution 5.0 Megapixel. Point counting was operated on at least 600 points for each thin section examined.

14C dating was performed on lime lumps and on the fine fraction of 45-63 μm from the bulk mortar. Samples were prepared using the sequential dissolution method.

3. Results and discussion

3.1 Petrographic examination

The mineralogy of the aggregates of all the analysed samples is substantially very similar, being composed of quartz both in individual crystals and polycrystalline aggregates, feldspars and plagioclases sometimes

ID	Sampling area	Analytical techniques	
		PLM	C-14
DIS_10_128	Painted (angular?) architectural decorative element	✓	
DIS_18_134	Painted architectural decorative element in relief	✓	
DIS_19_48	Painted decorative element	✓	✓
DIS_47_127	Painted flat decorative element	✓	
DIS_52_132	Painted decorative element	✓	
DIS_66_115	Painted decorative element associated with other fragments "in relief".	✓	✓
DIS_69_134	Painted decorative element with false inlays, part of a column	✓	✓

Table 1. Description of the analysed samples and analytical techniques used (PLM: Polarised Light Microscopy; C-14: C-14 dating).

exhibiting intense sericitization, phyllosilicates (biotite, muscovite, chlorite), metamorphic rocks (mainly-schists), granitoid rocks, and rare amphibolites. Opaque minerals are also present. The relative homogeneity of the aggregate used suggests that the sourcing area was the same for all the analysed mortars. The aggregate particle grading ranges between graded and well-graded medium-fine sands. Exceptions are the samples DIS_47_127 and DIS_52_132, which exhibit poorly graded aggregate particles.
The binder of all the samples is aerial lime composed of micritic calcite with frequent lime lumps.
The most notable difference is the binder-to-aggregate ratio (b/a). In particular, three main groups can be formed. In the first group the b/a is apx. 1.0 by volume (samples DIS_18_134, DIS_52_132, DIS_66_115, DIS_69_134; Figure 1A), 2.0 by volume (samples DIS_19_48, DIS_47_127), 3.0 by volume (sample DIS_10_128; Figure 1B). The differences in the proportion of the binder and aggregates can be explained by taking into consideration the technological features of the individual fragments though their exact contextualization in the original decoration is difficult. However, the execution of the angular element (sample DIS_10_128) may have required a more workable mix, justifying the higher b/a proportion. For the remaining fragments, a correlation is difficult to propose due to the unclear contextualisation of the individual findings. Taking into consideration that stucco decorations were constructed incrementally applying portions of material, a certain variation in composition may be expected. Further systematic analysis of comparable fragments is needed to ascertain the intentionality of the observed variations in the mixes.

3.2 14C dating
All the samples dated to the 8th century. Results for two samples (DIS_19_48 and DIS_69_134) showed a remarkable agreement between 14C obtained for lime lumps and fine fractions. The results are statistically identical and can be combined. However, one of the lime lumps (DIS_66_115) was slightly younger

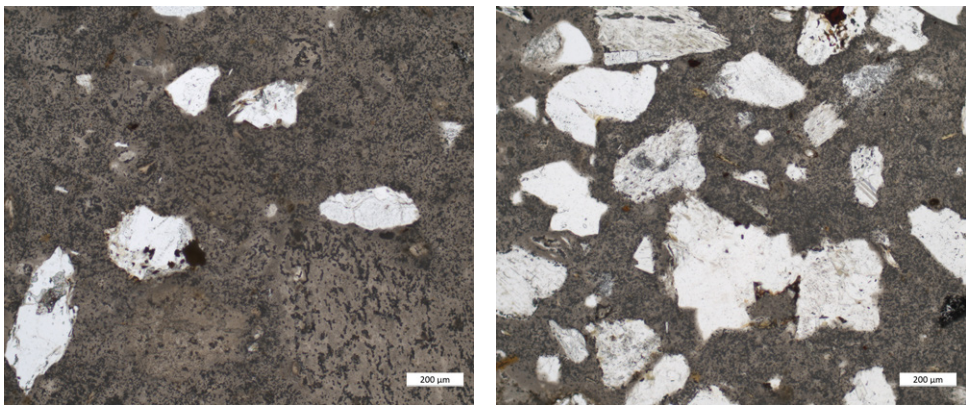

Figure 1. Different binder-to-aggregate (b/a) ratios in the samples DIS_69_134 (image A) and DIS_10_128 (image B). The absence of micro-cracks in the sample DIS_10_128 with b/a = 3.0 by volume is remarkable. Both images are in PPL.

and could not be combined with the corresponding fine fraction though the calibrated age was still in the range of 8th century. Since the fine fractions of all the samples are identical, it is possible that the lime lump contains some younger component. However, since the stucco was not exposed to the moisture and is near the surface, the potential recrystallization or late carbonation can be ruled out. Additional analysis of lime lumps from the same sample could help to clarify this offset.

4. Concluding remarks

The differences in the composition of the analysed samples from Disentis warrant further investigations, as possible functional groups could be formed by expanding the analysis to other plaster fragments. In addition, further in-depth considerations require the good microstructure of the samples with a higher b/a ratio that may be due to the addition of organic additives or the use of carbonate rocks containing clay minerals for lime production.

With an exception of one sample, radiocarbon dating of different fractions of plaster provides an excellent agreement of 14C ages. The slightly younger 14C age of the lime lump (DIS_66_115) might be due to later incorporation of younger CO2. The resulting ages coincide with the proposed date of the stucco decoration, which until now was based on inference from historical and archaeological data.

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YARDEN J. TSFONI, SIMONE DILARIA, ANDREA CIPOLATO, DANIELA COTTICA

Archaeometric Analysis of Structural Mortars from Sandrigo estate in Aquileia (UD)

1. Introduction

Aquileia, founded in 181 BC in northeastern Italy, was a key Roman city due to its strategic position on the Adriatic Sea and its river connections to the Eastern territories. Its long history, from the Roman Republic to the Early Byzantine period, saw multiple construction phases, making it an important site for studying ancient building techniques, particularly structural mortars[1]. Structural mortars for the present study include mortars used in the construction of walls, in particular. One such site is the Sandrigo Estate, located just outside the city walls along the Natiso cum Turro river, opposite the canal-port's monumental infrastructure. Since 2010, an interdisciplinary research project led by Ca' Foscari University of Venice has focused on this area, aiming to reconstruct the development of Aquileia's port system from its origins to its decommissioning[2].

2. Archaeological Context

Ongoing excavations by Ca' Foscari University of Venice in the Sandrigo estate (eastern riverbank of the Natiso cum Turro) are uncovering a complex interplay between human activity, the river, and the environment from the 1st century BC to the 6th/7th century AD. During the most recent excavation campaigns (2023-2024), the remains of significant buildings were uncovered, and their wall mortars were analyzed in this study. The site's evolution is marked by multiple construction phases, each associated with buildings of different functions, reflecting the site's transformation over time. The earliest remains belong to a villa rustica (Late Republic-2nd century AD): with N-S oriented rooms, built before the eastern shore had stone infrastructure. Continuous modifications suggest occupation from the Tiberian Age to the 2nd century AD. By the late 1st century, the riverbank was monumentalized, and the villa was reorganized around a central open courtyard. In the 3rd century AD, the villa was partially dismantled, likely for commercial purposes. Rubble deposits leveled the area for a new complex, incorporating pre-existing walls to form elongated rooms with L-shaped terminations, separated by passageways. A quadrangular basin with wooden partition impressions was installed alongside a drainage system in the open river-facing area. In the tetrarch period, a new structure replaced the earlier villa, featuring a large room divided by brick-founded pillars and bounded by a massive N-S wall. Its clay floor raised the occupation level by 50 cm. The pillar-supported warehouse (horreum) remained in use until the late 4th or early 5th century, when spoliation gradually stripped its structural elements.

3. Methodology and Results

The present research aims to characterize structural mortars from the sector of the 2023-2024 excavations of the Sandrigo estate to provide a better understanding of the chronology of construction phases

1 Dilaria 2024.
2 Cottica, Cipolato c.s.

and technological changes over time to supplement archaeological data on the phases of the site. Thirteen mortar samples were collected from walls pertaining to different building phases. Samples were analysed by optical microscopy (TL-OM XPL and PPL) and Scanning Electron Microscope-Electron Dispersive Spectroscopy (SEM-EDS) to characterize and categorize the mortars into groups based on their shared characteristics, thus providing information on the raw materials and techniques used in their production. Each group was, therefore, compared to various construction phases to verify the scan and evolution of the building phases of the site over time.

After in-detail analyses, two main groups as well as 2 outliers were identified. Group 1 (Figure 1a) is composed of a homogenous micritic lime binder with a relevant presence of lime lumps and a lean binder-to-aggregate ratio. Group 1 is complemented by a subgroup (Group 1b). This subgroup (Figure 1b) is composed of a homogeneous micritic lime binder, fairly smaller grain sizes of the aggregates, and fairly larger inclusions of lime lumps, which in the case of PR_31 are very large and abundant. For Groups 1 and 1b, the aggregates are similar. They are composed primarily of dominant and prevailing carbonatic clasts with the presence of both limestones and dolostones and a subordinate presence of chert and quartz, with chert prevailing over quartz: the aggregate Petromineralogical distribution is compatible with that of the Isonzo-Natisone-Torre alluvial sediments. Different from Group 1/1b, Group 2 is composed of a heterogenous micritic lime binder and the lime lumps are abundant. The aggregate is constituted primarily by lowly-fired ceramic fragments, reused mortars, and marble chips (Figure 1c and f). The two outliers exhibit significant differences from the previously described groups. PR_19 (Figure 1d) is characterized by an aggregate grain size that is in the gravel and sand categories, which is larger than the prior groups discussed. PR_35 (Figure 1, e) is a peculiar, earthen, and lime mix based mortar exhibiting scattered lime lumps and an absence of aggregates.

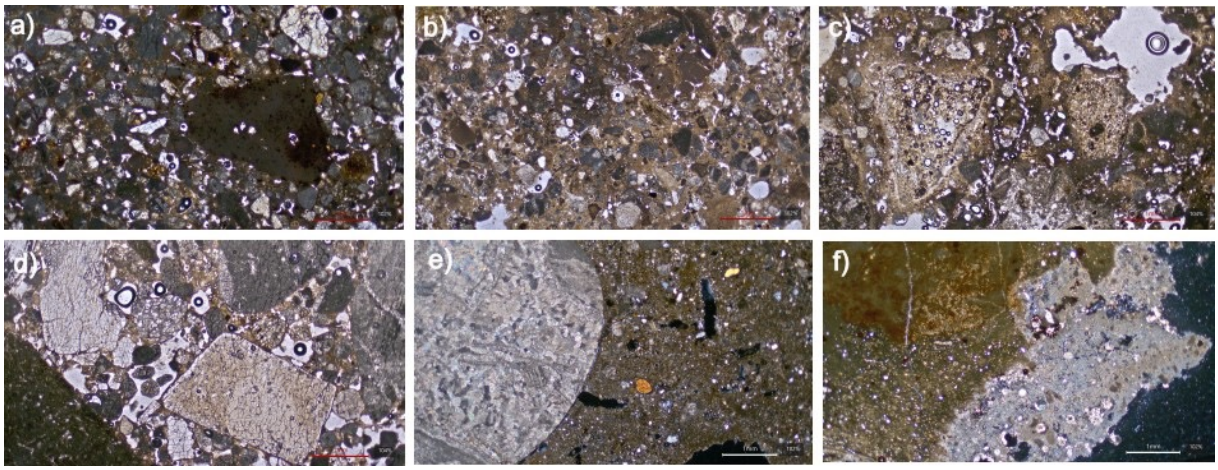

Figure 1. Thin section photos of the different groups of the mortar samples from the Sandrigo Estate under TL-OM, cross (XP) and plain polars (PP). a) Group 1, PR_33 (PP); b) Group 1b, PR_16 (PP); c) Group 2, PR_30 (PP); d) Outlier, PR_19 (PP); e) Outlier, PR_35; f) Group 2, PR_18 (XP).

The analysis of mortar groupings provides valuable insights into the different construction phases of the Sandrigo Estate. Unfortunately, Groups 1 and 1b correspond to two main phases: the initial construction of the Villa and the later addition of the Horreum (warehouse), built several centuries after the villa. Therefore, in this case, the standard and rather generic composition of the mortar in this group (lime and sieved river sand) did not allow for sufficient differentiation between these two phases. This highlights a limitation of mortar analysis when dealing with compositions that are entirely conventional and lack distinctive characteristics. On the other hand, for all other samples, significant clues have emerged that help clarify the construction sequence of the site. In particular, Group 2 aligns perfectly with the later phase of renovation of the villa, likely occurred in the 3rd century CE. Finally, the outliers belong to two distinct construction sub-phases. PR_35, for instance, is probably linked to a specific intervention involving the closure of an

Sample	Wall masonry USM	Phase (archaeological)	Chronology	Group
PR15	303	*horreum*	Late Antique	1b
PR16	603	*horreum*	Late Antique	1b
PR17	610	Main villa restoration	3rd c. AD	2
PR18	610	Main villa restoration	3rd c. AD	2
PR19	605	Villa construction (?)	End 1st – 2nd c. AD ?	outlier
PR21	608	Villa construction	End 1st – 2nd c. AD	1
PR25	606	Villa construction	End 1st – 2nd c. AD	1
PR29	720	*horreum*	Late Antique	1
PR30	725	Main villa restoration	3rd c. AD	2
PR31	734	Villa construction	End 1st – 2nd c. AD	1b
PR32	721	*horreum*	Late Antique	1
PR33	614	Villa construction	End 1st – 2nd c. AD	1
PR35	614b	Villa wall reconstruction	n.d.	outlier

Table 1 – analyzed mortar samples and their correlation to groups of building phases of the Sandrigo Estate.

opening in the villa at some point, possibly by filling in a portico or doorway (Table 1). Of particular interest is PR_19, which, while associated with the villa's masonry, stands out from the villa's typical mortars. Its distinctive composition (lime with a gravel aggregate) and the use of sandstone as a building material—unlike the limestone used in the villa's walls—suggest that this structure may predate the villa itself. The villa's walls appear to have been built in connection with this earlier structure. The use of gravel-based mortar and sandstone masonry recalls a construction technique prevalent in late Republican and early Imperial Aquileia .
In summary, the mortar analysis demonstrates how this method can significantly refine the chronological framework of an ancient site and complement archaeological data in defining construction phases.

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Characterisation of structural and lining mortars of the 'Terme a Mare' baths and the aqueduct in Nora (Italy)

1. The research and the contexts

This research presents the preliminary results of the compositional characterisation of the structural and lining mortars of two relevant Roman buildings in the ancient city of Nora (Sardinia, Italy). Specifically, the objects of the analysis are the thermal complex of 'Terme a Mare' and the aqueduct (2nd-3rd century AD), both of which share peculiar constructive features, that suggests they were built simultaneously during a phase of great urban development of the city during the Middle Imperial period and subsequently restored around the 5th century AD[1]. The 'Terme a Mare', situated close to the sea in the western part of Nora, were a monumental building equipped with a central frigidarium, and three heated spaces located in the north-western sector. The complex still preserves different rooms and some masonry structures, which are constituted with a facing of bricks of different sizes and opus caementicium cores, also visible in the collapsed vaults[2] (Figure 1, a). Monumental thermal complexes like these demanded a significant amount of water, making the development of a reliable water supply system absolutely essential. The urban aqueduct of Nora has not been entirely preserved, and most of the investigable evidence relates to pillars, arcades and the specus fragments scattered in the surrounding plain, no more than 1.5 km away from Nora, which are constituted by an opus caementicium nucleus and brick masonry facing (Figure 1, b).

Around 45 mortar samples were collected from both complexes, representing structural elements and render linings.

Figure 1: a) top view of the Terme a Mare (from Caneva, Dilaria 2024), b) preserved pillar of the aqueduct (photo taken by authors).

Most of the analysed samples are hydraulic mortars enriched with different types of pozzolanic aggregates that are primarily constituted by pyroclastic material such as pumices/tuffs or obsidians, or ce-

1 Bonetto 2018, 86-92; 117-118.
2 Previato 2023, 2.

ramic fragments. Several coarse samples of these volcanic aggregates have been selected to carry out geochemical analysis in order to define their provenance based on the comparison with the geochemical fingerprint of geological compatible volcanic products. The target of the research was to define the production technology, mortar recipes and determine the provenance of volcanic pozzolans on a geological basis.

2. Methods and preliminary results

Mortar samples and pozzolans were analysed adopting a multi-analytical protocol. Mortars were analysed, coupling Transmitted-Light Polarized Optical Microscopy (TL-OM) and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDS), providing a detailed characterization of their compositions and production techniques. Moreover, SEM-EDS together with XRF (X-Ray Fluorescence) were adopted to analyse the pozzolanic volcanic aggregates and to define their provenance based on the comparison with reference literature. The archaeometric analysis allowed us to investigate the petro-mineralogical compositions of each mortar sample, leading to the identification of four distinct mortar groups: a) aerial lime mortars; b) pumice/tuff-enriched limed mortars; c) cocciopesto enriched with pumice/tuff; d) cocciopesto enriched with obsidians. All binding mixtures are realized with a binder derived from the calcination of local fossiliferous calcarenite, and local silicate sands as main aggregates. Aerial lime mortar is largely attested in some of the structural pillars of the aqueduct and in few samples of the Terme a Mare (Figure 2, a). This compositional group presents an aggregate constituted by local sands with no pozzolanic component. Lime mortars enriched with pumices/tuffs (Figure 2, b) and pumices/tuffs-enriched cocciopesto (Figure 2, c) are present in both the aqueduct and in the bath's masonry structures and in the specus lining, while pumices/tuffs-enriched cocciopesto (Figure 2, c) and obsidian-enriched cocciopesto mortars (Figure 2, d) mortars are present only in hydraulic structures (vats) from the Terme a Mare. Regarding the provenances, SEM-EDS and XRF analyses allowed to establish that the trachy-phonolitc geochemical composition of pumices and tuffs is perfectly comparable with the one of the Phlegraean volcanic district, in the area of the Gulf of Naples[3]. Obsidian fragments, connoted by clear rhyolitic chemical fingerprint, most presumably come from the Monte Arci outcrop (southwestern Sardinia), whose exploitation in Nora for the supply of alternative pozzolanic materials has already been observed[4].

3. Conclusions

The use of various binding mixtures and pozzolanic aggregates, both local and imported, is widely documented in the mortars used in different buildings of Nora[5]. The primary results of this research concern the selection of raw materials: pumice-enriched lime mortars are mainly employed for structural functions (opus caementicium cores), while mortars constituted by pumice-enriched cocciopesto are primarily used for lining of hydraulic infrastructures and floor preparation layers. Pumices and tuffs from the Gulf of Naples were intensively imported for such purposes, showing long-range commercial trades between Southern Sardinia and Central Italy. Non-pozzolanic aerial lime mortars are attested in both complexes, some of them are employed in floor preparations although the majority could be related to Late Antique structural repairs of the original Middle Imperial installations. A particularly noteworthy practice is the use of cocciopesto mortars enriched with obsidian, which is found exclusively in the construction of a vat at the Terme a Mare. This could indicate the involvement of a specific local workforce dedicated to build this infrastructure. Ultimately, this production strategy suggests not only that different artisan groups contributed to the same construction project but also that the choice of distinct materials used as aggregate, sourced from regional and extra regional outcrops, was possibly linked to specific functional

3 Caneva, Dilaria 2024, 105-108.
4 The employment of obsidian aggregates in structural mortars is attested also in the Theatre of Nora (Columbu, Garau, Lugliè 2019).
5 Dilaria et al. 2023.

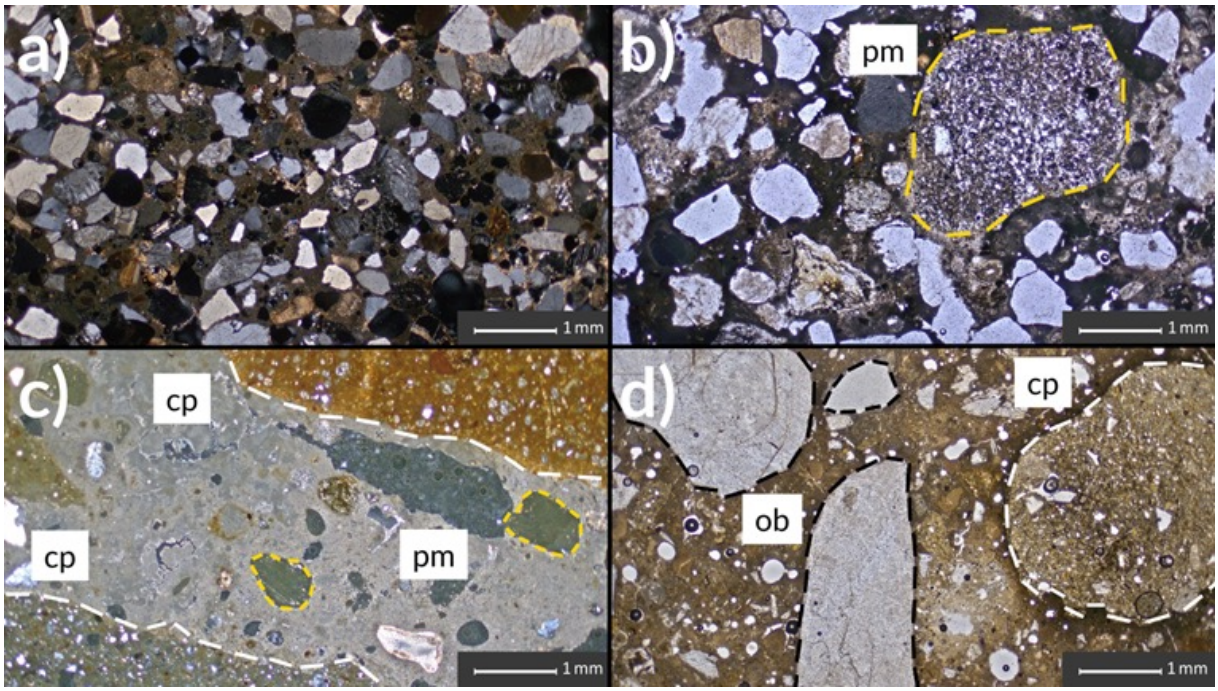

Figure 2: Detailed micrographs in polarised light microscopy, in transmitted light (TL) with crossed nicol (XN) and parallel nicol (PN); (a) representative sample of aerial lime structural mortar from the aqueduct (TL-XN), (b) representative sample of pumice/tuff-enriched lime structural mortar from the Terme a Mare (TL-PN), (c) representative sample of pumice/tuff-enriched cocciopesto lining mortar from the Terme a mare (LT-XN), (d) representative sample of obsidian-enriched cocciopesto structural mortar from the Terme a Mare (TL-PN). Legend: pm = pumice; cp = ceramic pozzolan; ob = obsidian.

purposes. These preliminary findings offer an overview on the production techniques of binding materials and the provenance of raw materials used in these distinctive contexts within the ancient city of Nora during the Middle-Late Imperial Period.

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Archaeometric study of mortars from the Roman Villa of Mutteron dei Frati, Bibione, Italy

1. Introduction

The Roman villa at Bibione di San Michele al Tagliamento, Italy, near the sandy relief known as the Mutteron dei Frati, has been a focal point of archaeological research since its discovery in 1760. Key investigations, including those by Bertolini (1903)[1], Cassi (1932), and the Superintendency of Padua (1991), have provided important preliminary insights into the site's historical significance. Excavations have revealed two construction phases: the first, dating from the 1st century BCE to the 1st century CE, characterized by meticulously built limestone walls bound with mortar and substantial foundations, and the second, from the 4th–5th century CE, featuring walls built with reused limestone fragments and brick fragments[2]. Recent excavation campaigns (2022–2024) have uncovered additional architectural elements and provided mortar samples for scientific analysis.

2. Materials and methods

This paper presents an archaeometric analysis of mortar samples from the Villa Bibione, employing a range of analytical techniques, including colorimetry, X-Ray Powder Diffraction (XRPD), petrographic analysis via Transmitted light Optical Microscopy (TL-OM) coupled with Digital Image Analysis (DIA), and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS). These analyses, contextualized through a review of historical and archaeological literature, aim to reconstruct the composition, production techniques, and chemical processes involved in the manufacture, setting, hardening and ageing of the mortars. The results contribute to a deeper understanding of Roman construction practices and know-how, offering new insights to scan and periodize the building activities of this coastal settlement during the classical period.

3. Results and discussion

The results of the study allowed us to identify 3 main groups of mortars and two outliers that can be associated with different construction and restoration phases. Group 1 consists of wall mortars with uniform characteristics. These mortars are rich in lime content, with several lime lumps and an aggregate represented by medium-fine sands rich in carbonate content, and no reused mortar particles (Figure 1a). They group mostMost of the sampled wall structures, indicatingsamples belong to this group, representing an early, consistent construction phase, with no significant compositional variation and identifying the original conformation of the villa. Group 2 is defined by leaner wall mortars with a higher aggregate content and the presence of gravel (Figure 1b), clearly differing from Group 1 mortars. The samples pertaining to this group cluster in the southern part of the villa, and belong to the porch enclosure, suggesting a later restoration phase, are possibly linked to the closure of an open porch or to the modification

1 Bertolini, 1884.
2 Busana 2002.

of the villa's structure. Group 3 features wall mortars with reused particles and a slightly higher dolomite content (Fig.Figure 1c), pointing to restoration or a later construction phase of restoration occurred during Late Antiquity. As notable outliers, samples WM_11 and WM_22, show distinct characteristics that suggest they belong to earlier construction phases., antedating the construction of the villa. Sample WM_11, coming from a wall structure positioned at a lower heightlevel of the villa, containing a calcination relict, is likely related to an older structure, antedating the construction of the villa (Figure 1d). Sample WM_22, - with its leaner composition and higher porosity, also appears to belong – likely belongs to an earlier construction phase, as supported also by itsthe wall orientation and stratigraphic position. Additionally, floor preparatory layers show evidence of different production techniques, with those from the Group 1 lacking the utilization of cocciopesto, and samples PREP_07 and PREP_09 from the Group 2, originating from the southeastern part of the villa, including cocciopesto and possibly indicating later restoration efforts.

4. Conclusions

In conclusion, the analysis of mortars reveals the villa'sfrom the Roman villa of Mutteron dei Frati can be one of the methods to reveal the villa's multiphase development, with the earliest phase (pre-villa) marked by yellow, (outliers), the main constructive phase in dark blue, (Group 1), the porch enclosure in green (from which Group 2 mortars come from), and the later wall restorations, pertaining to group (Group 3) in light blue (Figure 2). Additionally, floor preparatory layers show evidence of differing construction techniques, with Group 1 lacking cocciopesto, while samples PREP_07 and PREP_09 from the southeastern part of the villa include cocciopesto, possibly indicating later restoration efforts. Figure 2). These findings provide a comprehensive understanding of the villa's evolving construction history, materials sourcing, and changing buildingvariation of mortar preparation techniques across different phases, reflecting both initial construction and subsequent restoration activities.

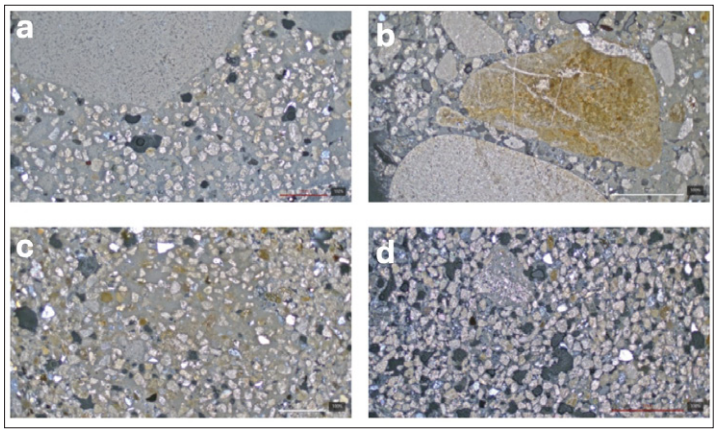

Figure. 1. a) mortar sample from the Group 1 (TL-OM, crossed polars), b) mortar sample from the Group 2 (TL-OM, crossed polars), c) mortar sample from the Group 3 (TL-OM, crossed polars), d) outlier mortar sample (WM_11) (TL-OM, crossed polars)

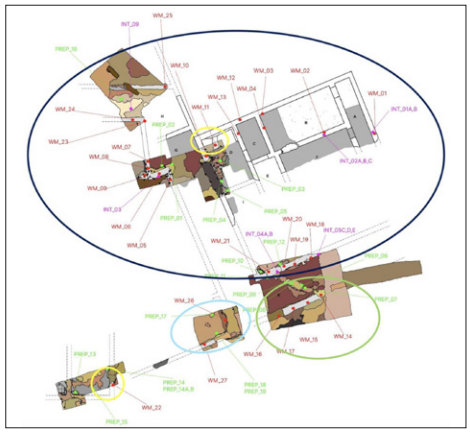

Figure 2. Mortar sampling points from the excavation campaigns 2022-2024 and hypothesis on construction phases

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Plasters and wattle and daubs from the Domus dei Dolia (Vetulónia, Italy). An archaeometric study

1. The archaeological context

The Domus dei Dolia was discovered in 2009, in the Etrusco-Roman neighbourhood of the ancient town of Vetulonia (Castiglione della Pescaia Town Hall, Southern Tuscany, Italy). Archaeological evidences interpretation made possible the documentation of an almost entire Etruscan - Roman house, probably occupied between the 3rd and the 1st century BC [1]. Different materials were collected during several archaeological campaigns between 2009 and 2015, including ceramics, plasters, votive bronze statues, coins, nails, charred woods, wattle and daub, unfired bricks, roof tiles, in addition to several big earthen pots (i.e. Dolia) inside the storage room (Room A, Figure 1) of the Domus.

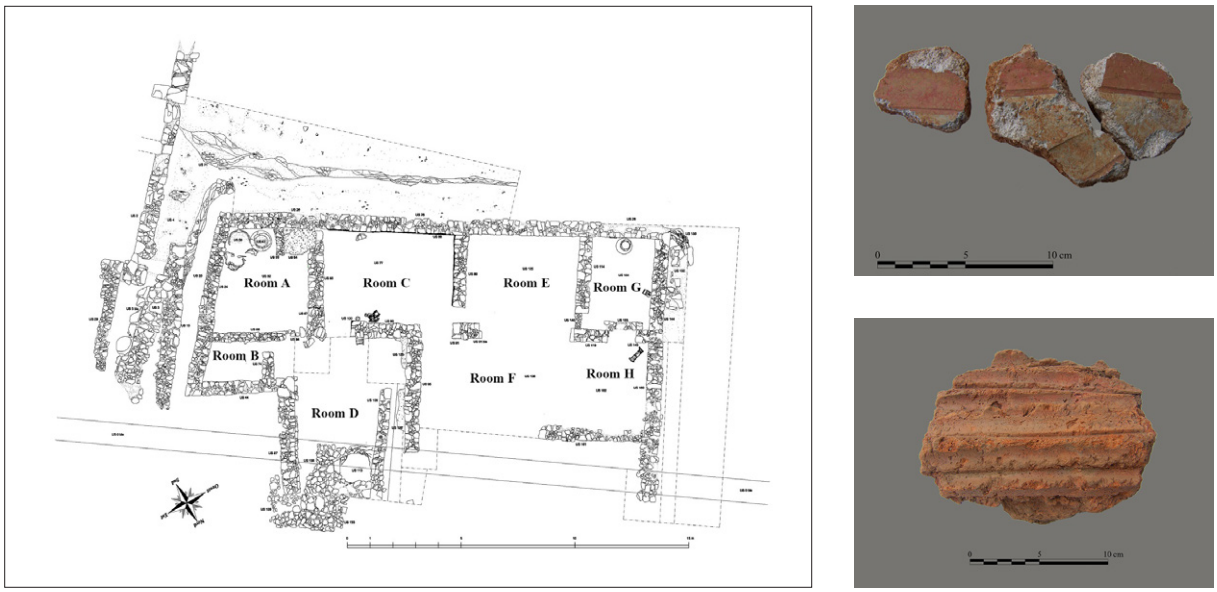

Figure 1. Planimetry of the Domus of the Dolia, and the divisions brought to lightafter different archaeological campaign carried out between 2009 and 2015. At the top-right, some fragments of plasters, with red and light blue plasterspaint. At the bottom-right, the back side of a wattle and daub fragment.

2. Research aims

The objectives of the study are: 1)To characterize the production recipes of plaster and wattle and daub fragments; 2)To determine the "recipe" employed in terms of binder and aggregate characteristics for mortar and wattle and daub production; 3) To understand the manufacturing technique and the technology employed; 4) To define the technique used on pictorial layers; 5) To define the pigment used on pictorial layers; 6) To increase our knowledge of Etruscan architecture.

3. Materials and methods

In total 16 different samples of plasters (11) and wattle and daub (5) were considered in this study, and they were collected during the archaeological excavations carried out between 2009 and 2015. Samples were recovered from three different subdivision of the Domus (Figure 1), namely from the storage room (A), from the triclinium (i.e. the formal dining room - C), and from the tablinum (i.e. representative guest reception room - E). Room C and E were characterized by the presence of black, red, light blue, and yellow mural paintings belonging to the first Pompeian style. Although plasters identification was straightforward during the archaeological excavation, the classificationidentification of the earthen architectural materialmaterials, as wattle and daub, was confirmed byobserving the presence offragments back side where wooden beam like traces on the back side of the fragments.were clearly visible (Figure 1). The study involved a multy-analytical approach including, optical microscopy, x-ray diffraction (powder and micro-mode), digital image analysis, thermogravimetric analyses, micro-analysis by SEM-EDS, μFT-IR spectroscopy, and pyrolysis-gas chromatography coupled with mass spectrometry.

4. Results, so far

The study is not concluded yet, and different evaluations are still on-going. Specifically, pigment identification has not been completed yet, and it is not possible to state whether an organic binder was utilized in pigment application. In any case, it is possible to summarize the most representative results so far. Plasters were mainly composed by two different layers, the intonaco and the arriccio. The intonaco consists of very angular calcite crystals which suggest the use of milled recrystallized limestone/marble. Quartz aggregates are rare and, when present, the grain size is very small. The binder, light brown in color under crossed polarized light, had a homogeneous appearance in all cases with micrite-like texture mainly composed by micro and crypto crystalline calcite (confirmed by SEM-EDS and TGA). The second one, the arriccio, showed two different recipes. In the first case (siliciclastic arriccio), aggregates are mainly silicates, prevailing quartz over feldspars and lithics (sandstones, slates, cherts), being still observed nodules of lime. The shape of the aggregates is quite rolled suggesting a significant transport, probably corresponding to a river sand. In the second case (cocciopesto arriccio), the aggregate mostly consists of quartz, plagioclase feldspars, potassium rich feldspars, muscovite, clinopyroxene, and opaque minerals (rare) crystals. Siliciclastic rock fragments were less represented. In contrast, it was enriched in brick/tile fragments (i.e. containing clinopyroxene and plagioclase feldspars inclusions) and mafic aggregates. In both cases the binder is identical to the intonaco layer.

Wattle and daub samples showed two different layers. Considering a lack of definitions for this specific class of material, we decided to classify identified layers as intonaco, and arriccio (i.e. similarly to plasters). The two layers look very similar, but they mainly differ in thickness and aggregates grain size, being the arriccio layer thicker, and with smaller aggregates. In both cases rounded to sub-angular equant inclusions

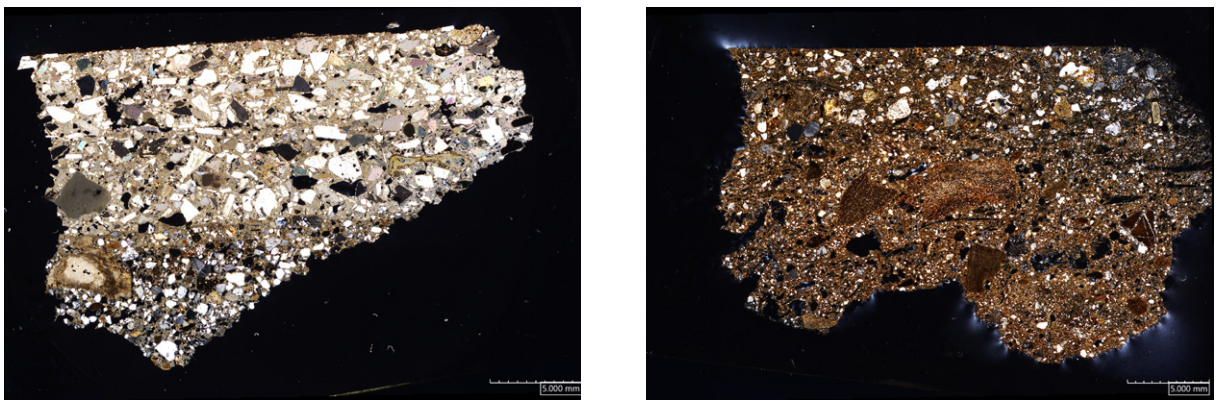

Figure 2. Digital microscope image of the whole thin section of samples ETR-3 (Sample of plaster with siliciclastic arriccio layer), and ETR-11 (wattle and daub sample). Different intonaco and arriccio layers can be clearly observed in both cases.

were dominant, mainly consisting of quartz, plagioclase feldspars, potassium rich feldspars, muscovite, biotite, and opaque minerals (rare). Siliciclastic rock fragments (i.e., sandstone, siltstone, claystone, calcarenite) were common. Granitic rock fragments were also rarely observed. Optical microscopy evidenced that the binder/matrix is homogeneous, completely composed by clay, light brown when observed in crossed polarized light, and with a moderate optical activity. Nevertheless, carbonates (i.e. calcite) were detected both by XRD and TGA, suggesting that some lime was probably added to the original recipe in both cases.

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New insights into the composition of provincial Roman mortars – Lederata fort in Serbia

1. Introduction

Frontier of the Roman Empire consisted of a series of military fortifications, along which civilian settlements and infrastructure were built with life flourishing in all its aspects, transforming the landscape into a place of exchange, interaction and connection between people. It stretched over 7,500 km, and in today's Serbia, the border followed the Danube River in its length of 588 km[1]. During the MoDeCo2000 project, mortars from 24 Danube sites in Serbia were sampled (mostly bedding and core mortars), dated to the period from the 1st to the 6th century, to design compatible conservation mortars[2]. Additionally, raw materials (lime, schist, clay, and natural brick) were collected from sites assumed to have been exploited by Romans. In this presentation, a very brief overview of the results of the research on a particular core mortar is given, which stood out due to its exceptional mechanical features and durability and brought new understanding of mortars from the Roman period in the territory of today's Serbia. The mortar belongs to a rampart of the first Lederata military fort phase built during the Trajanic period, in the beginning of the 2nd century (Figure 1a).

Figure 1. a. Remains of the 2nd century walls from Lederata (left), b. Mortar sample fragments and a cross-section (photos of the MoDeCo2000 project)

2. Materials and methods

During the project MoDeCo2000, the following methods and techniques were applied in the research of historical mortar samples: visual inspection (mortar condition; colour; aggregate, binder and their ratio; impurities, lumps, fibres, etc.); determination of the physical-mechanical properties (density; porosity with particle size distribution; capillary water absorption; compressive strength; adhesion to the substrate); determination of the mineralogical-petrographic composition; determination of the chemi-

1 Korać et al. 2014.

2 Delić-Nikolić, Miličić, Nikolić 2024; Nikolić et al. 2023; Vučetić et al. 2022; Vučetić, Ranogajec 2022. This research was supported by the Science Fund of the Republic of Serbia, PROMIS, #6067004, MoDeCo2000.

cal composition; and thermal analysis. Firstly, grouping of samples in those belonging to the structures whose research is important for various conclusions in terms of archaeology, and those belonging to structures whose conservation was planned in the near future, was conducted. After visual inspection and the analyses of its physical-mechanical properties, a core mortar of the Lederata fort rampart was analysed using TL-OM, SEM-EDS, XRPD, Raman spectroscopy, FTIR, XRF, DTA-TG, and DSC-TG-MS. Various analyses of this sample were conducted on its three separate fragments, by three institutions in Serbia and Italy (Figure 1b)

3. Research results

The sampled mortar of the Lederata fort rampart was bound to a fragment of schistose metamorphic rock, used as exclusive building stone for the fort, on whose bed the fort itself was built and which crushed fraction represents the primary mortar aggregate in all fort phases (2nd - 6th century). The fat lime mortar sample, dated to the 2nd century, showed a high value of compressive strength (15.7 MPa) and an overall high level of preservation and durability, having a bulk density of 1.429 g/cm^3, total porosity of 33.7% and open porosity of 19.06%. Using optical microscopy, abundant lumps of unmixed lime were detected, while calcination relics were almost absent. Reaction rims around the aggregates were almost absent or just feeble around the feldspars. The mineralogical analysis of the bulk sample, as well as of the binder-concentrated fraction, revealed relevant reaction products showing the significant hydraulic reaction of the mortar and indicated the employment of a natural hydraulic lime as a binder[3]. The same was concluded by SEM-EDS analyses of the bulk sample and the lump cores. XRF analyses of the bulk sample offered the ratio of the values of CaO+MgO (32.20%) and SiO2+Fe2O3+Al2O3 (50.54%) as 1:1.6, commonly interpreted as B/A. However, the similar ratio of soluble to insoluble part of 1:1.5 obtained by chemical separation was further complemented with the treatment of the insoluble part, that showed the amount of soluble silica as 8.37%, indicating the use of an hydraulic binder and leading the modification of the preliminary B/A ratio to 1:1. FTIR analyses of the binder-concentrated fraction (<63 μm) reported it was based on CaCO3 with aluminosilicate bonds, but also that the abundant lime lumps were CaCO3 and silicates. Loss of the structurally bound water, as well as the CO2/H2O ratio, determined by thermal analyses, showed the high hydraulicity of the mortar.

4. Concluding remarks

Although it was planned by the MoDeCo2000 project that only the most prominent Roman sites along the Danube Limes in Serbia in terms of historical, archaeological or architectural value should be sampled, mortars from all available sites were collected – in order to get data that probably would not have been obtained by examining only mortars selected according to any chosen heritage valorisation criteria (which is in line with the known issue of achieving representativeness in the sampling[4]). Examination of the mortar from the partially archaeologically investigated Lederata fort with little published data, and consequently not adequately valorised and protected site, brought some of the most significant project results. One of the oldest dated and best-preserved project mortar samples, with the highest compressive strength value among them all, is a true example of the use of local materials in Roman building practice. Precisely because of this and the results indicating the hydraulic nature of the sample binder, the search for the origin of the lime used for the fort building became extremely important, as well as the extension of the detailed research to the mortars from all its construction phases. We hope that future research on Roman mortars will bring new data on the ways of achieving their durability in the sites where common natural materials with pozzolanic features were not readily available, such as those in the area along the Danube here presented.

3 Dilaria et al. 2023.
4 Hughes, Callebaut 2002, 72-73.

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The use of volcanic pozzolans and tuffs in Roman Villas of the Tuscan Archipelago: The Villa of the Domitii Ahenobarbi at Giglio Island. Preliminary Analyses

1. Introduction and target of research

In the Tuscan Archipelago, several Roman villae, both villae maritimae and otium villae, have preserved structural remains dating back to the Late Republican and Early Imperial periods (1st c. BCE – 1st/2nd c. CE). These residences were initially built by influential Roman families, especially the gens Domitia and the Domitii Ahenobarbi, before becoming imperial properties. The buildings are characterized by construction techniques typical of central Tyrrhenian Italy, particularly opus reticulatum and opus mixtum (reticulatum combined with brickwork). Notably, some of these techniques employed non-local volcanic materials, such as tuff and pozzolanic aggregates, for both the facing stones and the concrete cores—materials that are absent on the islands themselves. This is evident in the Villa Domizia on Giannutri, the villa of the Domitii Ahenobarbi on Giglio, and the Villa of Agrippa Postumus on Pianosa. These construction practices suggest an organized trade network supplying volcanic materials, from central southern Italy, a phenomenon already known for mainland southern Tuscany[1]. Archaeometric analyses have confirmed this aspect for other Roman coastal structures, such as the Portus Cosanus and the villa of Santa Liberata/Domitiana positio near Porto Santo Stefano[2]. Additional analyses on the Villa of Giannutri also indicate the presence of leucite-rich volcanic cinerites (likely from Si-undersaturated volcanism, e.g. Colli Albani south of Rome), included in mortars as pozzolanic aggregates[3].

A research project led by the University of Siena in collaboration with the University of Padova is investigating the diffusion of opus reticulatum and opus mixtum in southern Tuscany, both considering building techniques and the chemical-mineralogical composition of stone-based and mortar-based materials[4]. The working hypothesis is that this architectural knowledge—along with skilled labor and materials—was introduced through the initiative of powerful Roman patrons. Over time, this led to the local adoption and adaptation of these techniques in coastal and possibly inland sites across Tuscany. Initial archaeometric investigations, here presented, have focused on volcanic-based masonry from the villa on Giglio Island, associated with the Domitii Ahenobarbi and emperor Nero.

2. The case study: the Villa at Giglio Porto (building phases and techniques)

The original layout of the villa maritima at Giglio Porto (Figure 1), likely commissioned by Lucius Domitius Ahenobarbus, dates back to the late Republican period. The villa, at least in its residential part, is organized on two main levels: at sea level, there are several rooms built in opus reticulatum and opus mixtum, including a fishpond (piscina) and a monumental semicircular terrace, above which stands a quadrangular building supported by massive substructures in opus caementicium faced with reticulatum. In the area of

1 Marra et al. 2015.
2 Brandon et al. 2014, 63-73, 243-253.
3 Bonazza et al. 2006.
4 We would like to thank the ABAP Superintendency for the provinces of Siena, Arezzo, and Grosseto, and in particular Dr. Enrico Giuffrè, for kindly granting permission to carry out this study.

Figure 1. Location of Giglio Porto; concrete and opus mixtum structures built with volcanic materials.

Castellare, the remains of a hexagonal lighthouse built in opus reticulatum are preserved. Additionally, in the northern area of Giglio Porto, another complex includes terracing walls and a probable nymphaeum. Based on several archaeological evidence, a series of renovations has been identified, occurring between the Neronian period, and the Flavian-Trajanic and Hadrianic eras[5]. While most of the structures were built using local granite, other walls (such as a room at Cala Saraceno, the nymphaeum, and adjacent structures) are constructed in opus reticulatum and opus mixtum using urban bricks and tuff lithotypes that do not correspond to the island's local geology.

3. Archaeometric analyses and preliminary results

15 mortar samples and 15 stone samples from opus caementicium structures were collected from the Roman villa at Giglio Porto with the aim of characterizing the materials employed and determining their geographical provenance. These samples were subjected to a comprehensive multi-analytical protocol, including Transmitted Polarized Light Optical Microscopy and X-ray Powder Diffraction (XRPD), in order to define the petro-mineralogical composition of both mortars and stones. In addition, the stone materials and coarse volcanic aggregates were analyzed using X-ray Fluorescence (XRF), which proved crucial in tracing their origin by comparing their geochemical fingerprint with existing geological data from the literature. Preliminary results have shown that, alongside the use of local granite, often shaped into small blocks for opus reticulatum or crushed as aggregate in mortars, as seen in the fishpond structures, other materials were also utilized. Notably, in particular in the nymphaeum, opus reticulatum walls were realized by tuff blocks. The associated mortars are enriched with coarse and fine grained yellowish-grayish pumiceous pozzolans (Figure 2, a), presumably attributable to the Neapolitan Yellow Tuff or post-NYT formations of the Phlegraean Fields in the Gulf of Naples. Furthermore, in some of the opus caementicium structures of the nymphaeum, the presence of cineritic tuffs caementa was recorded.Yellow tuffs were likely sourced from the same sources of the volcanic pozzolans in the Gulf of Naples (Figure 2, b), while other tuffaceous facies likely originate from the volcanic districts of central Italy, such as the Colli Albani (Tufo Lionato, Figure 2, c) or the Mount Sabatini/Vico districts (Figure 2, d). These findings reveal a complex construction strategy at the Roman villa on Giglio Island, suggesting not only the selective use of imported materials but also the integration of the site into a wider network of trade in building materials involving central and southern Italy. This evidence aligns with similar phenomena observed at other villas in the Tuscan Archipelago, supporting the hypothesis of skilled builders, likely trained in Campanian-Latium construction traditions, being involved in the villa's construction. In addition to the adoption of opus reticulatum, the architectural and material choices reflect the influence of elite Roman patronage and further emphasize the high-level investment behind this monumental complex

5 Rendini, Bigagli 2011, with referenced literature.

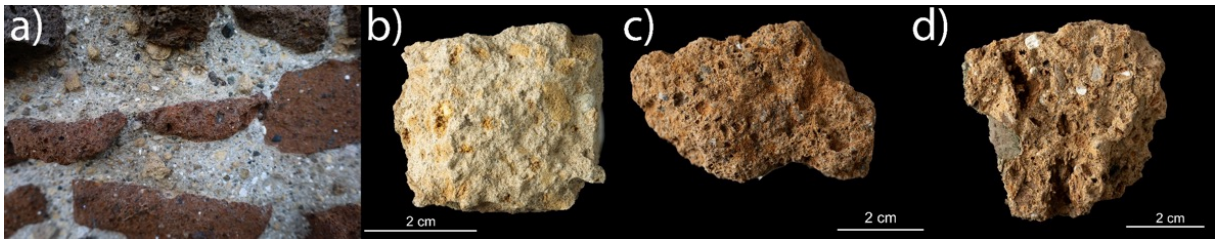

Figure 2 - Volcanic materials used in construction: a) Pumice-enriched mortar; b) Yellow tuff – originating from the Gulf of Naples; c) Reddish tuff from Colli Albani (Tufo Lionato); d) Scoriaceous reddish tuff from southern Etruria (Tufo Rosso a Scorie Nere).

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Novel evidence of exploitation of Euganean Volcanic Breccia for Roman pozzolanic mortars uncovered by bridging together archaeometry with UAV-LiDAR

1. Introduction

By interacting with lime-based binders, volcanic pozzolans played a crucial role in enhancing the mechanical properties of ancient mortars and concretes. From these reactions, hydrated calcium-silicates, hydrated calcium-aluminates, or hydrated calcium-aluminosilicates can develop, contributing significantly to the strength and hydraulicity of these construction materials. Ancient authors, including Vitruvius (2.6.1; 5.12.2) and Pliny (NH 35.166), documented the use of volcanic pozzolans, distinguishing between two primary types: the cinerites of the Pliocene eruptions of the Colli Albani (harena fossiciae), which were widely used in mortars in Rome and the Lazio region from the Middle-Late Roman Republican age onward; and the pulvis puteolanus, referring to pumice and unconsolidated volcanic tuffs from the Neapolitan Yellow Tuff and post-Neapolitan Yellow Tuff formations of the Phlegraean Fields, extensively employed in Roman construction and traded throughout various regions of the empire from the Augustan period onward. However, in the peripheral regions of the Roman Empire, builders often substituted traditional Vitruvian pozzolans with locally sourced volcanic materials exhibiting similar pozzolanic properties. This practice demonstrates their sophisticated knowledge of construction materials and regional geological resources. Notable examples include sources in Turkey, Sardinia and Rhineland (Trass)[1].

2. The case study

In this paper, we present a novel case of alternative pozzolan utilization, emerged from the analysis of mortar samples from the archaeological site of Via degli Scavi in Montegrotto Terme (Padua, Italy) (Figure 1a). Several mortar samples were collected from thick opus caementicium foundations and cores of the wall masonries and were fully analyzed via Transmitted-Light Optical Microscopy (TL-OM), X-Ray Powder Diffraction (XRPD) and SEM-EDS. Most of the samples demonstrate a pozzolanic character being composed of lime mixed with fine and coarse volcanic aggregates (Figure 1b). These aggregates, identified as breccias of trachyte-trachyandesite chemical composition, have been confidently attributed to the nearby Euganean Hills volcanic district based on their general petro-mineralogical features. The Euganean district is characterized by extensive volcanic and subvolcanic lava flows, primarily erupted during the Oligocene, with compositions ranging from rhyolitic to basaltic. Among these, the trachytic lava variety was widely used as construction material during the Roman era[2]. Additionally, the district contains volcanic deposits from submarine diatreme eruptions, rich in Si-rich amorphous components and potentially suitable as pozzolanic additives for mortars. However, no evidence of their ancient extraction or use has been documented until now.

1 Dilaria, Secco 2022.
2 Zara 2018.

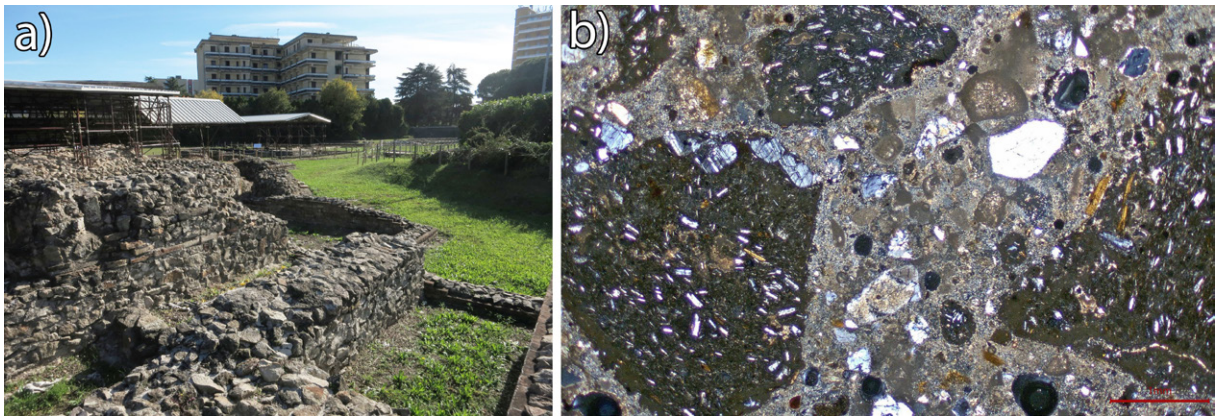

Figure 1 – a) The archaeological site of Via Scavi in Montegrotto (PD); b) optical microscopy micrographs (transmitted light, crossed nicols) of clasts of the pozzolanic volcanic breccia aggregates in the mortars.

3. The methodology and results

To better investigate the potential extraction of Euganean volcanic breccias for mortar production, we conducted detailed geological surveys and sampling campaigns, focusing primarily on the explosive diatreme districts of the Euganean territory. A key outcome of our research was the discovery of previously unknown, now-abandoned quarry sites used for extracting volcanic breccia and other stone types, whose historical cultivation was not reported in the 20th century cartographies of the Euganean historical quarry sites[3]. High-resolution UAV LiDAR technology was instrumental in this discovery, enabling the detailed mapping of quarry sites across an 8.5 km² area in the southeastern area of the Euganean territory. The LiDAR surveys identified around 90 potential extraction sites, uncovered previously undocumented anthropogenic features, and facilitated the creation of precise digital terrain models (DTMs) at a resolution of 0.2m² to identify new ancient quarry sites and differentiate them from modern ones. These findings were crucial in guiding geological sampling efforts at the identified sites: numerous samples were collected and analyzed from such abandoned quarries using a multi-analytical approach, including TL-OM, XRPD and X-Ray Fluorescence. The resulting data were then integrated into an existing geological database of Euganean volcanic products, developed in-house by researchers from the Department of Cultural Heritage and Geosciences of the University of Padova, comprising over 250 Euganean volcanic rock samples from various lithologies and sources within the district. The origin of the volcanic pozzolans in the Montegrotto mortars was determined by comparing the petrographic, mineralogical, and geochemical characteristics of volcanic rock samples from the database with the distinctive features of the pozzolanic clasts embedded in the mortars. The coarser ones (> 3 grams) were extracted from the samples and analyzed as they are. A direct correspondence was found with the trachytic breccia from the Villa Draghi quarry—a site that emerged as a crucial source of pozzolanic additives for Roman construction. This quarry is distinguished by peculiar textural features and unique geochemical fingerprints, such as an exceptionally high Sr content, which completely overlaps with the geochemical fingerprint of the pozzolanic clasts (Figure 2a). The extension of the Villa Draghi quarry, now abandoned and overgrown with vegetation, was reconstructed through UAV LiDAR surveys (Figure 2, b-c), revealing an intensive cultivation, with significant volumes of material extracted across more than 750 meters of quarry fronts. This study highlights the effectiveness of integrating high-resolution LiDAR with archaeometric analysis to reconstruct historical quarrying activities. By mapping extraction sites, analyzing their morphology, and tracing materials to their geological origins, the research offers new insights into the exploitation of pozzolanic materials in the ancient world.

3 Calvino 1967.

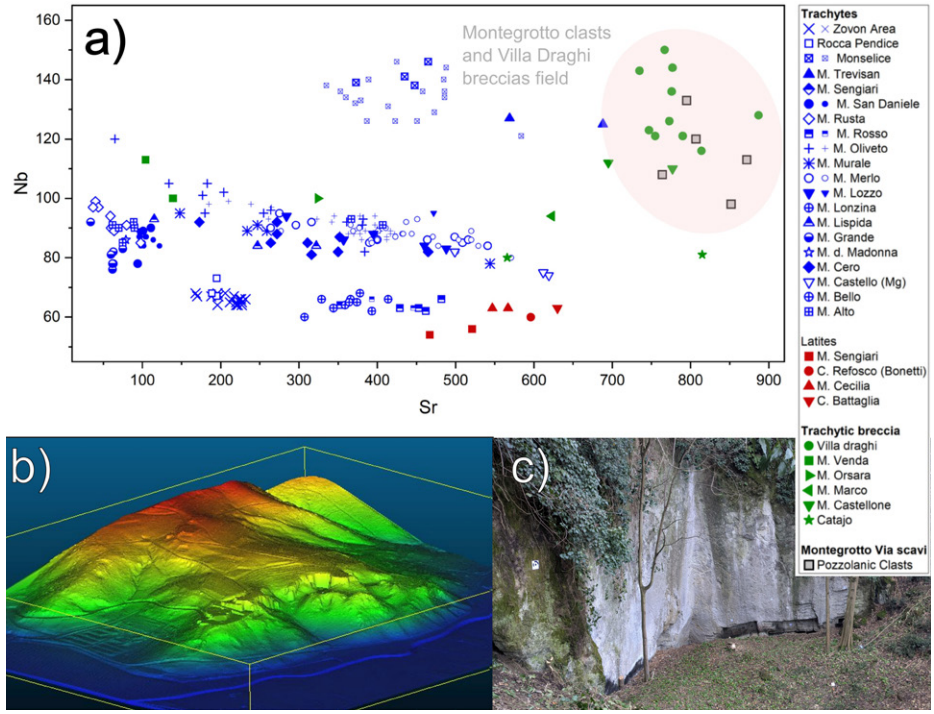

Figure 2 – a) Geochemical matching of Montegrotto volcanic pozzolans with Villa Draghi outcrops (Sr vs Nb Scatterplot). Geological reference points plotted from the in-house database; b) the LIDAR UAV survey of Villa Draghi quarry and c) On-site inspection of quarry features of the site.

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Study of Ancient Multilayer Render from Archaeology remains of 4th CE UNESCO World Heritage Site

1. Introduction

Mortars are composite materials made of a binder and aggregates, used since ancient times as structural and binding elements. Early civilizations like Mesopotamia, the Indus Valley used mud and lime mortars in monumental buildings. In masonry, mortars serve as jointing agents, plastering layers, and external renderings. Renderings play a critical role, as they protect masonry facades from weathering and help create impermeable surfaces in areas exposed to humidity. Systematic analysis of historical mortars—some several hundred or even thousands of years old—has shown that they have withstood the test of time, resisting deterioration caused by aging, natural disasters, mechanical damage, moisture-drying cycles, and freeze-thaw effects. Mortars characterized by such durability continue to perform their structural functions even today. Despite the lack of formal technical documentation, the enduring performance of these mortars highlights that durability depends not just on strength but also on the craftsmanship of ancient builders.

This study investigates the ancient multilayered renders, from the archaeological remains of Nalanda Mahavihara, a UNESCO world heritage site and a prominent Buddhist monastic centre that flourished between the 3rd and 13th centuries CE. The site features remain of multi-storeyed buildings and renders that have survived in remarkably good condition. These remains exemplify a rare combination of advanced material science and exceptional craftsmanship from ancient times. This work aims to provide new data on the composition of raw materials used in the multi-layered renders, along with an evaluation of construction techniques that reflect the technical proficiency of skilled artisans from the Gupta and Pala periods of ancient India.

2. Methodology

The renders observed at this site are lime-rich and were applied in multiple layers. The thickness of each layer ranges from a few millimetres up to 20 mm, with the innermost layer being the thickest (12-20 mm) and the outermost the thinnest (4-6 mm). To avoid damaging the ancient walls, 20–30 g samples were carefully collected. The render layers were precisely separated for analyses. Acid reaction test using HCl was first performed. Then, binder-to-aggregate ratio of each individual layer was analysed using microwave digestion system[1]. Optical observation of thin-sectioned was carried out, followed by Digital Image Analysis (DIA) to quantitatively evaluate textural parameters. The semi-quantitative mineral composition was determined using X-ray diffraction (XRD), and Rietveld refinement was performed to compare the composition across layers. While Fourier transform infrared spectroscopy (FTIR) was employed to identify functional groups, including possible organic additives. Thermal characterization was carried out using thermogravimetric Analysis (TGA) and differential thermogravimetry (DTG), which provided insights into their hydraulic properties. Additionally, the pore structure of the render was examined using mercury intrusion porosimetry (MIP).

1 Rampazzi et al. 2006.

3. Results and Discussion

Visual, chemical and microscopic observations suggest that the multi-layered render of lime was applied following a clear sequence or set of rules. The compact transition zones between layers, visible in microscopic images (Figure 1), confirm the stability of the render matrix. The binder-to-aggregate ratio ranged from 1:0.5 to 1:0.8, with the outer layer containing more binder than the inner coat. Optical and DIA analyses show the use of angular and fine aggregates, with the outer layer containing finer particles. Microscopic images further confirm the presence of fine brick fragments and silicate aggregates. XRD and Rietveld refinement results (refer Figure 1), indicate a relatively high amount of calcite in the outer layer ranged between 60 to 75 %, along with common non-reactive minerals such as quartz, feldspar, and traces of calcium silicate hydrate and calcium aluminate hydrate, pointing to a hydraulic character of the render [2]. FTIR analysis (Figure 1), supports these findings and confirms the presence of organic materials and proteins. TGA results indicated that the CO2/H2O ratio was less than 4, ranging between 2 and 3.5, with a hydraulic water content between 7% and 10%, suggesting that the render had a highly hydraulic nature[3]. This implies that the binder was likely prepared artificially, using either air lime or natural hydraulic lime mixed with pozzolanic material to enhance its hydraulic characteristics. MIP results indicated that, from the innermost to the outermost layer, the render becomes progressively more compact, leading to a reduction in porosity, critical pore diameter, and threshold pore diameter, thereby effectively limiting moisture entrance into the masonry[4].

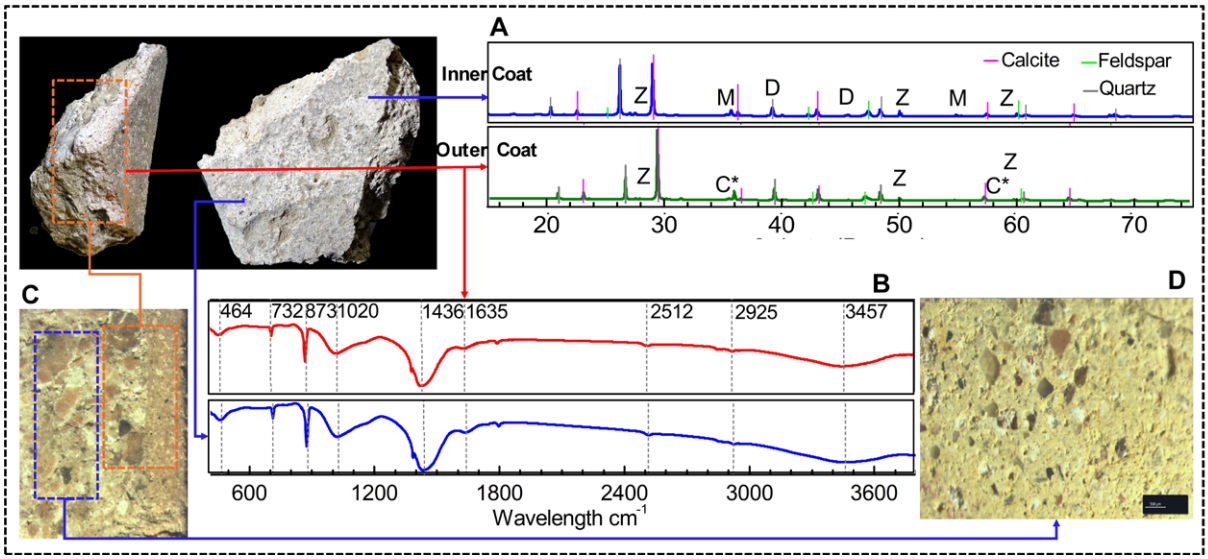

Figure 1. Compositional analysis of the multilayer render (A) XRD graphs of the inner and outer layer showing the identified binders and aggregates minerals (B) FTIR graphs showing the obtained functional groups peaks (C) Microscopic image showing the compact bonding between the layered render (D) Microscopic image of inner coat [M-Muscovite, D- Diopside, Z- Zeolite, C*-Calcium Silicate Hydrate]

The results suggest that a highly durable render was achieved by incorporating lime with pozzolanic materials such as brick dust, which imparted hydraulic properties. From the inner to the outer coats, the lime content increased while the aggregate size decreased. The use of finer aggregates and higher lime content improved particle packing, resulting in a denser, more cohesive matrix that facilitated smoother surface finishing and enhanced resistance to moisture entrance. In terms of performance, carbonation typically progresses more slowly from the exterior to the interior due to the increasing diffusion path

2 Anand et al. 2025.
3 Moropoulou et al. 2000.
4 Nogueira et al. 2018.

length for CO_2 and pore structure densification in the outer layers after initial carbonation[5]. However, the use of thinner coats promotes more complete carbonation throughout the render thickness. Additionally, interfaces between layers serve as barriers to environmental degrading agents and help prevent continuous cracking through the entire depth of the render. These findings offer valuable insight for durable rendering techniques for heritage conservation.

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5 Benedetti et al. 2003.

MARTA CAROSELLI, GIACINTA JEAN, FRANCESCA PIQUÉ

Material Analysis and Relative Dating of the wall paintings in the Baptistery of San Giovanni, Riva San Vitale (Ticino)

1. Introduction

The Baptistery of San Giovanni in Riva San Vitale (Switzerland) is a remarkable example of early Christian architecture, dating back to the 5th century. Inside, it houses some of the oldest mural paintings in the Canton of Ticino, created between the 9th and 13th centuries. These artworks are layered in a complex stratigraphy and are only partially preserved.

Since 2019, the Master's program in Conservation and Restoration at SUPSI has the opportunity to plan and develop a conservation intervention on these paintings. The students' work focused on gathering essential information to understand past and present problems that impact their preservation. The study on materials and artistic techniques also offered an opportunity to discover new elements that contributed to the attribution and dating of the decorative phases to specific historical periods.

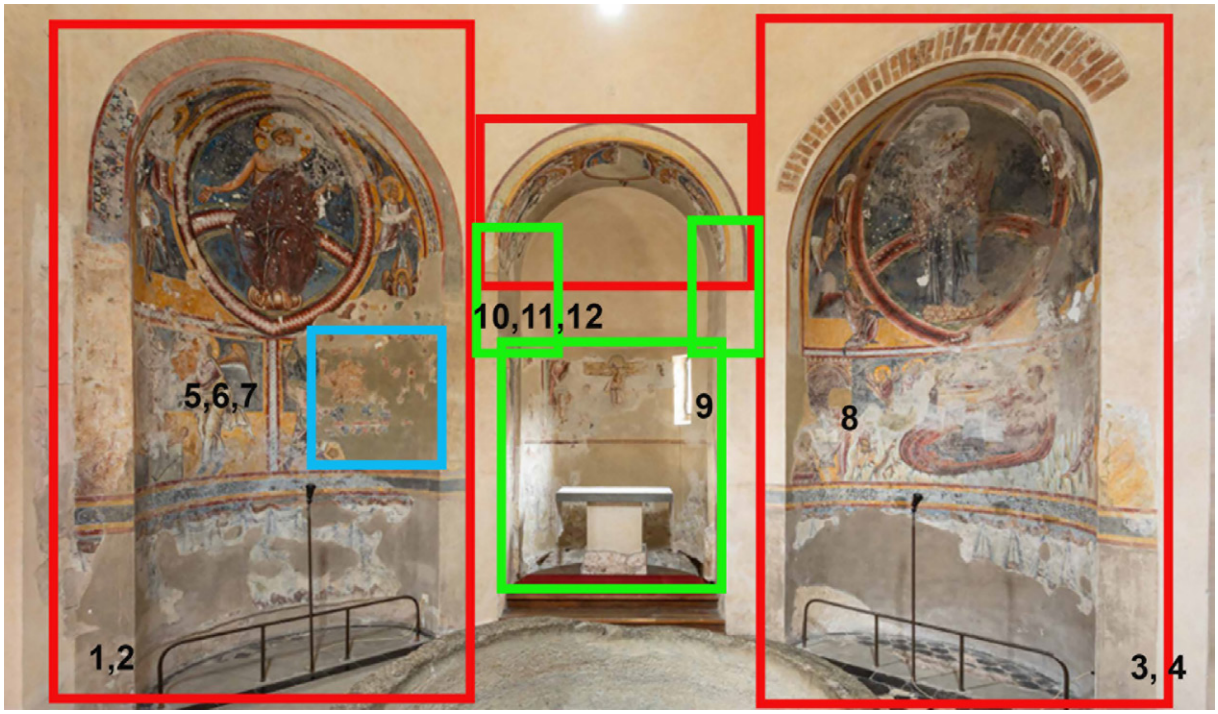


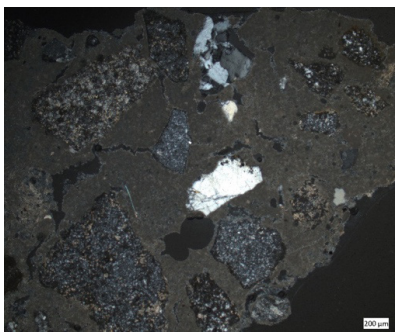
Figure 1. Interior of the baptistery with the decorative phases: green rectangles - paintings attributed to the 10-11th C.; blue rectangle – fragments of paintings attributed to the 12th C., red rectangles - paintings attributed to the 13th C. The numbers indicate the position of the samples. Picture by Alberto Canepa from Bettini et al. modified.

2. Materials and methods

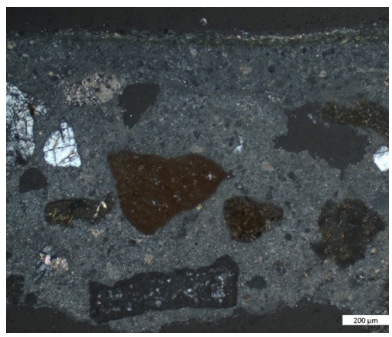
The team of conservator-restorers conducted a detailed visual examination to determine the painting methods and materials of the different decorative phases. Following non-invasive investigation sampling was carried out. In terms of plaster analysis, a total of 12 samples of painted plasters were collected (Figure 1), prepared as thin sections, and analyzed using a Zeiss Axioskop 40 petrographic microscope. The samples were taken from: the white-colored plasters at the base of the walls near the two entrances (samples 1, 2, 3, 4); the oldest painted plasters including the velarium decoration (sample 12), the simple floral motifs around the small window in the apse (sample 9) and within the sub-arch (sample 10). In the northeast (NE) niche, all three existing plaster layers were sampled: the earliest painted layer, only partially visible (sample 7); an intermediate, whitewashed plaster layer (sample 5) and the outermost painted layer, dating to the 13th century (sample 6). In the southeast (SE) niche, only the outermost layer was sampled (sample 8).

Table 1

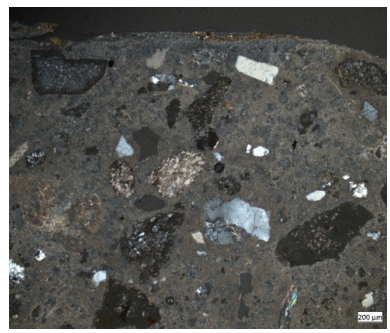
Comparison of photomicrograph XPL of thin sections of the plaster samples of the earliest phase (10-11th C.)



a) Sample 12

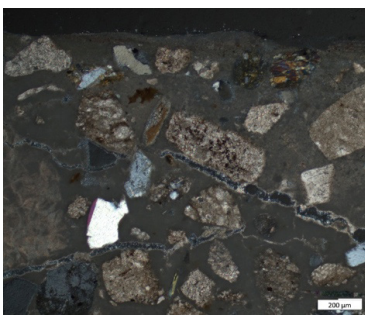


b) Sample 9



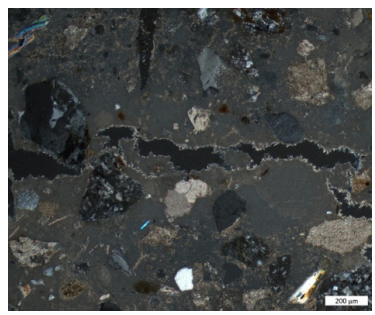
c) Sample 10

Comparison of photomicrograph XPL, of thin sections of the plaster samples of the 13th C. phase



d) Sample 6

e) Sample 8



f) Sample 11

3. Results discussion and conclusion

The results of the analyses were surprisingly interesting: within the same building, the materials and painting techniques changed throughout the decorative phases (Table 1). The differences found are very useful in cases of uncertain dating and when only fragments of painted plaster remain, making stylistic attributions difficult while the plaster characterization is possible.

Petrographic analyses have shown that the plasters next to the entrances attributed to the first phase of the baptistery, the oldest paintings in the apse and the first painted layer in the NE niche have a similar composition (Table 1, Figs. a,b,c). Here the magnesian lime binder is partly hydraulic, due to the use of reactive cherts. It is unclear whether the chert was added as an aggregate or whether it was an impurity of

the dolomitic limestone used to produce the binder and was therefore also heat treated. The cherts grains show reaction rims, and the surrounding binder has become hydraulic. The painted layer of samples from these phases is yellow or green with the use of ochre-based pigments.
On the other hand, the painted plaster in the later niches (13th century), in the underlying layer found only in the NE niche, and in the painting of the Virgin in the sub-arch, all have a similar composition (Table 1, Figs. d, e, f) containing a local sand aggregate with a predominantly limestone composition. The pink and yellow paint layers are made with an ochre-based pigment. In addition, hydromagnesite is highly diffused in the N-E niche on the different layers of plaster. Hydromagnesite is a by-product of neoformation due to deterioration linked to prolonged exposure to water.
Further diagnostic studies would make it possible to apply absolute dating of mortars on the different phases of decoration and provide useful information for reconstructing the appearance of the Baptistery over the centuries.

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LARA MARITAN, ANNA BREDA, ISABELLA FINZI CONTINI, LISA SANTELLO, JACOPO NAVA, FRANCESCA SIMI, DANIELE MORANDI BONACOSSI

Traces of color/paint on the rock-reliefs of the Assyrian irrigation system at Faida and Khinis (Iraqi Kurdistan)

1. Introduction

The impressive water-management system built in the eighth-seventh century BC by the Assyrian king Sennacherib in the hinterland of Nineveh, on the left bank of the Tigris river in Mesopotamia (Iraqi Kurdistan), consists of a network of hundreds of kilometers of artificial channels created for irrigating the plain of the ancient capital of the Assyrian Empire[1]. This irrigation network testifies to the enormous power of the king which is celebrated, at the head of the channel system and along its course, by commemorative monumental rock-reliefs carved on the Eocene dolostone constituting the bedrock of the area.

During the extensive cleaning and restoration of these reliefs, carried out within the Land of Nineveh Archaeological Project (LoNAP) in the archaeological sites of Khinis and Faida, numerous micro-samples were collected to analyse the reliefs' surfaces that in some points were very compact and smoothed, and brown-reddish. The main purpose of the study was to define if this compact surface was the result of a natural alteration of the rock or if it was related to the possible presence of an applied coating.

A set of 17 microsamples, 8 from the reliefs of Faida and 9 from that of Khinis, were collected and analyzed by stereomicroscopy (using a Zeiss Stemi 305 microscope equipped with an Axicam 208) and scanning electron microscope (using a Teschan Solaris FEG-SEM), and some of them also by micro-Raman spectroscopy (using a WITec Alpha 300 R equipped with a 532 nm laser) and X-ray powder diffraction (using a Philips X'Pert PRO equipped with a Co radiation and X'Celerator detector).

2. Results

The analysis at the stereomicroscope and especially that at the scanning electron microscope indicated that the samples from the reliefs are composed of two different portions. The dolomitic rock on which the reliefs were carved, is characterized by a micro-porous structure with portions showing a very intense networking of voids and microfractures, as well as some occasional micro-fossils. On the top of that, in all the samples collected from the reliefs, there is a very fine-grained calcite layer, corresponding to a limewash. The high-resolution micro-stratigraphic analysis indicated that this limewash is composed of numerous layers, each with a thickness of a few micrometers, often showing a carbonation surface (marked by a denser material), indicating that between the application of one layer and the subsequent one, at least a few hours passed (Figure 1). This microstructure is typical of application such as those used for the fresco in wall paintings[2].

Moreover, in the most external layer of the limewash, traces of red earth are also preserved. Small crystals of hematite associated to flakes of phyllosilicates, quartz and feldspar, are embedded in the calcite layer, indicating that the red earth was applied while the limewash was still wet, according to a fresco technique. Samples of the bedrock, collected near the reliefs, show the absence of calcite deposits on the surface of the dolostone, as well of clay minerals and iron oxides.

1 Morandi Bonacossi 2018, 77-115.
2 Piovesan et al. 2012, 723-736.

3. Conclusions

Both the reliefs of Khinis, continuously exposed to weathering throughout the centuries since their creation, and those of Faida, covered by the passive infilling of the channel by sediments after its abandonment after the collapse of the Assyrian Empire in 612 BC, preserved fragments of the limewash, documenting for the first time traces of fresco and painting on Assyrian rock-reliefs and its application technique.
This finishing technique was probably used to provide more resistance to the relief's surface, exposed to the atmospheric weathering agents, as well as prepare a substrate on which to apply a color to the magnificent and impressive sculptures, that could be seen also from distance.
The panels were frescoed with a deep red colour which was polished, thus obtaining a shiny surface. In the Assyrian language this chromatic effect is described by the adjective ruššû, "having a reddish-golden sheen". In the Assyrian texts, the term is associated with deities or kings to describe the divine or royal radiance, the dazzling aura pervading gods and kings. We probably have to imagine the Faida and Khinis rock reliefs as red shiny frescoed surfaces glittering from afar, thus expressing the immense power of the Assyrian deities and kings.

Figure 1. Left – detail of the relief of Faida; right - SEM-back scattered electron image of the stratigraphy observed in one of the fragments collected from the relief of Faida, in which the dolomitic rock on which the reliefs were carved is covered by layers of very fine-grained calcite,

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ANDREJA SIRONIĆ, NIVES DONEUS, MATHIAS MEHOFER

Influence of the Mediterranean climate on mortar degradation in archaeological monuments

1. Introduction

The Croatian part of the Adriatic coast holds archaeological monuments preserving valuable historical information. The objective physical information of about the monument's construction date is contained in its mortar, and this information can be obtained by means of radiocarbon dating. Mortar radiocarbon dating is, in itself, subjected to a number of preconditions, and the maritime influence (Mediterranean climate) further complicates its application. Because of it, the mortar in the monuments is subjected to degradation by: mechanical destruction by strong winds, high humidity, the influence of water and the introduction of sea salt, which crystallizes to further absorb water – thus destroying the structure of the mortar and enabling calcite recrystallization.

In this research, a comprehensive approach was taken to evaluate the influence of mortar degradation on the possibility of acquiring accurate 14C dates from such samples.

2. Methods

The study area of archaeological interest was the Roman city of Osor and its surroundings, on the islands of Cres and Lošinj in the Kvarner Bay, northern Adriatic. A total of 22 mortar samples were taken from selected monuments and classified according to their distance from the coast and the influence of the sea. Physical methods used to evaluate the condition of the samples prior to 14C radiocarbon analysis were SEM (salt content), thin section petrography (occurrence of calcite recrystallization) and XRD (magnesite content). 14C dating was conducted on samples without calcite recrystallization and magnesite content, applying the principle of extrapolation after sequential dissolution[1-2]. Also, if charcoal remains were found in samples, they were used as anchor for mortar dates.

3. Preliminary results

The SEM results point to the metal content of the samples. Higher Na, Cl and S contents were observed in the samples near the coast, or on the higher levels with more influence of sea winds. Calcite recrystallization was noted in similar samples, but more related to the influence of water (e.g. samples taken below the surface levels). Neither Na nor Cl content were solely observed in samples with recrystallization and therefore cannot be used as its indication. Magnesite content was observed in only two samples, with no specific relation to marine influences.

1 Sironić et al. 2023.
2 Sironić et al. 2024.

4. Data synthesis

The results of the physical and 14C analyses will be contextualized within a historical framework and subsequently evaluated in comparison with the urban development of the Roman city of Osor and the architectural heritage of the surrounding area. Project results aim to establish a standardized methodology that can be applied to other similar monuments. In doing so, we hope to benefit also archaeological research and facilitate a broader discussion on the mortar analysis in archaeological research.

Acknowledgement

The research was funded by the two-year project "Mortar analyses of archaeological monuments in the Mediterranean climate regions" within the bilateral Technical Cooperation between Austria (Federal Ministry of the Republic of Austria) and Croatia (Ministry of Education and Science) and carried out in cooperation with the project "Osor beyond the myth", funded by the Austrian Science Fund (FWF): Grant-DOI: 10.55776/I6039.

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Topic 4

Historic renders and plasters. Gypsum-based plasters and mortars. Adobe and mud mortars. Rammed earth constructions. Natural and Roman cement mortars. Assessment

CATARINA BRAZÃO FARINHA, ROSÁRIO VEIGA, ANTÓNIO SANTOS SILVA, JOEL MOEDAS-MIGUEL

Characterization of the interior and exterior coating materials from 18th and 19th century of Casa do Moscadim. Case Study

Casa do Moscadim is a 18th-19th century manor house located in Chamusca, Portugal. Three main construction and decorative periods can be identified in the house: 1760s (construction of the original building and first period of mural paintings and tile decorations); 1790s (second decorative campaign); and 1880s (third decorative campaign). The architecture, construction type and materials are representative of the historical periods, building typology and region in which it is located. In its interior, the tile panels from the 18th and 19th centuries stand out, bonded with air lime mortars, generally in the most important rooms and in the staircase, as well as mural paintings from these periods. The tiles come from the royal factory "Real Fábrica do Rato". All these aspects contribute to giving the house a notable cultural and historical value.

Figure 1a. Casa do Moscadim: general vue of the façade.

Figure 1b. Casa do Moscadim: detail of an interior panel of glazed tiles at Moscadim staircase.

The house had some constructive interventions over the centuries which contributed to its preservation over generations. Presently, the house needs maintenance over again. The use of materials and techniques similar to the original ones and compatible with the existing ones will contribute to a greater longevity of the House's original identity and its overall durability.
This study was based on the will to develop, with Casa do Moscadim, a project that would constitute an example of the need to study the original materials before beginning any architectural restoration and

rehabilitation intervention, of an historical heritage building. An initial characterization of the materials applied in the coatings is essential, both for historic registration and interpretation and for a future conservation.

To identify the coating materials of Casa do Moscadim, several mortar samples were collected and analysed in laboratory. The samples included several coats of render mortars, tile laying mortars and decorative gypsum plasters. In the interior of the house, samples from two interior rooms were characterized (Breakfast room and Dinner room) and from the staircase wall (Moscadim Staircase). From the façade two samples were collected and analysed, including from the wall socle.

Chemical, mineralogical, physical and mechanical tests were carried out on the samples collected. The chemical and mineralogical characterization tests included X-ray diffraction, thermogravimetric and differential thermal analysis, as well as chemical analysis tests to determinethe determination of the content and grain size distribution of the sand. For the physical and mechanical characterization, modulus of elasticity test, water absorption test and compressive strength testtests were performed.

The results of the chemical and mineralogical characterization indicated that all the interior mortars (both plasters undercoats and tile laying mortars) were composed by similar materials: dolomitic lime as binder and siliceous sand as aggregate[1]. Finishing plasters were composed by lime (Breakfast Room)[1] or lime and gypsum (Moscadim Staircase)[1], with compositions typical of traditional Portuguese decorative gypsum plasters of the period[2]. The render mortar from the façade was the richest in lime content of the whole, possibly to better resist the external environment, and the topcoat applied was composed by dolomitic lime[1].

The physical and mechanical performance of the interior mortars depended on the samples analysed. The test results are summed up in Table 1. In general, the samples richer in binder presented superior mechanical characteristics and lower water absorption[3], but in some cases this relationship was reversed, probably due to degradation caused by water and the presence of salts or by movements of the substrate, or even by aspects related to the application[3]. However, it is considered that their mechanical and physical performance is appropriate for this type of coatings, with the exception of the most degraded samples.

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1 Santos Silva et al. 2024.
2 Freire et al. 2019.
3 Veiga et al. 2024.

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JEREMY MISTRETTA

Tadelakt: An ancient technique amidst modern times

1. Restoring history through science

Morocco is the birthplace of "tadelakt," a lime plaster process and design trend that has swept the modern world. With its inherent depth, rich history, dynamic color, and cultural significance, it's no wonder that walls across the planet are now being coated with this coveted technique. In April of 2025, (10) practicing tadelakt artisans from around the world, armed with their formulaic version of the craft, visited the North African village of Ighels and worked alongside local craftsmen to restore the walls of a 500-year-old once mosque and shared their formulas, knowledge, and technique. The effort ensured that the community, the tadelakt practice, and structure could thrive in their original form for centuries to come. Due to its rise in popularity, many installations outside of Morocco have come under scrutiny due to their imitative components. Authentic tadelakt installation varies drastically from the modern and streamlined iterations

Figure 1

found globally, although it still produces similar resulting characteristics of thickness and water absorption rates. Figure 1 highlights the restored columns of the Ighels structure.

2. Complexity of application and diverse formulas

At its baseline, tadelakt is a lime plaster that's integrated with olive oil soap and polished with a smooth river stone in a timely manner. Tadelakt walls are hydrophobic and have become a gleaming homage to both societal success and application in modern day wet areas of homes. Traditional Moroccan lime, specifically "Marrakech" lime is burned in a kiln at temperatures that reach 850-1300 degrees Celsius. While the tamarisk trees used to fuel these kilns embed remnant ash into the resulting quicklime, it's important to note that these perceived impurities serve as an integral aggregate with varying grain distribution that act as a filler to eliminate excessive shrinking in the resulting hydraulic render. In other parts of the world, as noted by our participants, readily available hydrated limes and varying sizes of marble or silica sands integrate to form slightly thinner blends with the aggregate, but still act as building blocks, providing the structure required to form a hydrophobic render[1].

3. Accelerated approach to an ancient technique

Moroccan hydraulic lime has a fast initial set, and gains strength over time through a constant exchange of moisture, yet due to its rigid characteristics, the render will inevitably crack. While thinner gauged imitative plasters composed of flexible hydrated limes have a slower set, they ultimately dry faster and gain strength quicker through the absorption of carbon dioxide, allowing for lasting installations in modern construction that is free of cracks. These renders inevitably produce faster and longer lasting results, while maintaining the hydrophobic qualities necessary to call the material a tadelakt, making it a viable protective coating option for present day homes around the globe[2].

4. Strengthening of craft through exchange of knowledge

As advancements in technology push building timelines, craft stands in jeopardy. Ancient structures like the mosque, steeped in cultural heritage and technique, provide insight into local methodologies and need to be celebrated. Moroccan tadelakt is one of these techniques as its authentic chemical components can be replicated worldwide, producing similar end results in both form and function. The material transcends domestic barriers, and its gatherings and intended efforts like the Ighels passion project that will continue to preserve their place in history.

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1 Aguilar et al. 2019.
2 Amrani et al. 2018.

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Macro- and microstructural characterisation of rendering mortars from the 18th century Fishing House of the Recreational Farm of Marqueses de Pombal (Portugal)

1. Introduction

The Casa da Pesca (Fishing House) is an 18th-century complex located within the Recreational Farm of Marqueses de Pombal in Oeiras, Portugal. The complex is located in the northern part of the farm and consists of the main house, surrounding gardens, the Taveira waterfall, and a pond. In 1940, the Casa da Pesca complex, along with the gardens and the Marquês de Pombal palace, was classified as a National Monument[1], thus becoming subject to the protection and safeguarding regulations for cultural and built heritage. Due to the historical and cultural significance of the complex, the City Council of Oeiras requested the National Laboratory for Civil Engineering to conduct an extensive macro- and microstructural characterisation of the Casa da Pesca rendering mortars. The goal was to analyse the original renders and paintings and assess their characteristics and performance, in order to support the design of appropriate and effective future conservation and intervention measures.

2. Materials and methods

With the aim of characterising the constitution, composition, conservation state, and performance of the renders, several samples were collected from the Casa da Pesca complex and tested at both macro and micro levels. To determine the stratigraphy and evaluate the pictorial layers, samples were observed using a stereozoom microscope and analysed with scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). To evaluate their functional capacity and conservation state, physical and mechanical characteristics were assessed through several laboratory tests, which were developed and validated in previous studies[2-3]. These tests included capillary water absorption by contact (EN 15801), dynamic modulus of elasticity via ultrasound, compressive strength (EN 1015-11), and open porosity (NP EN 1936).

3. Results and discussion

3.1 Microstructural characterisation

The rendering mortars studied generally consist of four layers: (1) a calcium aerial lime-based mortar with a cream-orange colour, containing siliceous and carbonate sand aggregates with traces of clay minerals, possibly of marine origin due to the presence of shells in its composition, with a binder/aggregate ratio between 1:5 and 1:5.5 (by mass); (2) a mortar with a composition similar to that of the first layer but lighter in colour; (3) a white calcium lime-based stucco; and (4) a lime-based paint finishing layer, typically consisting of a single coat with pigments of mineral origin (likely natural earths), ranging in colour from red-ochre to yellow-ochre (Figure 1). The first two layers – 1 and 2 - are present in all the samples collected.

1 DGPC. 2020.
2 Veiga et al. 2004.
3 Valek and Veiga 2005.

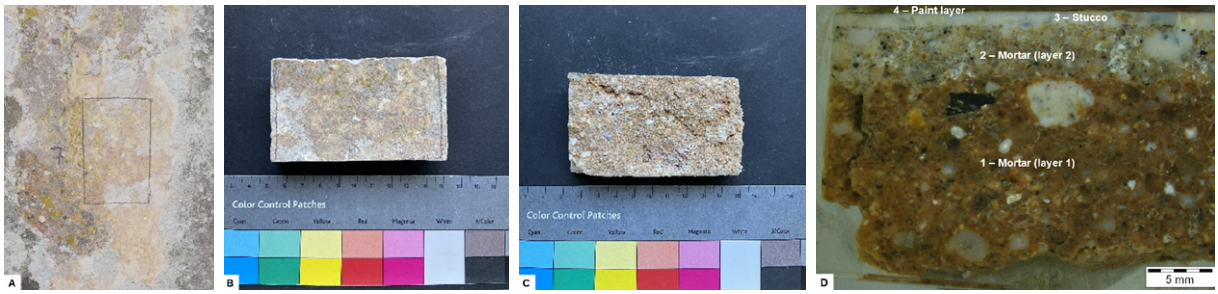

Figure 1. Collection area for one of the samples from the north-facing wall of the staircase (A); external (B) and internal (C) faces of the rendering mortar collected from (A); and stereozoom microscope image of the rendering mortar sample (D)

Some of the rendering mortars collected from lower areas like the wall of the staircase on the side of the Casa da Pesca, the wall to the north of the pond, and the plinth of the north façade of the Casa da Pesca lacked the stucco and paint layer in their composition. These stratigraphic differences, particularly the absence of the stucco layer, could indicate areas where conservation or repair work has been performed, or they may suggest that different application techniques were used in these areas. Additionally, on the north façade of the main house of Casa da Pesca, where a red ochre-coloured paint layer was identified, an area with multiple colours has been observed, with the oldest layer containing ultramarine, blue pigment (Figure 2A). Based on this finding, it cannot be ruled out that this façade was originally decorated with some type of drawing (mural painting). A similar pattern seems to have existed on the south-facing gutter wall, where the paint does not appear to form a continuous layer (Figures 2B and 2C).

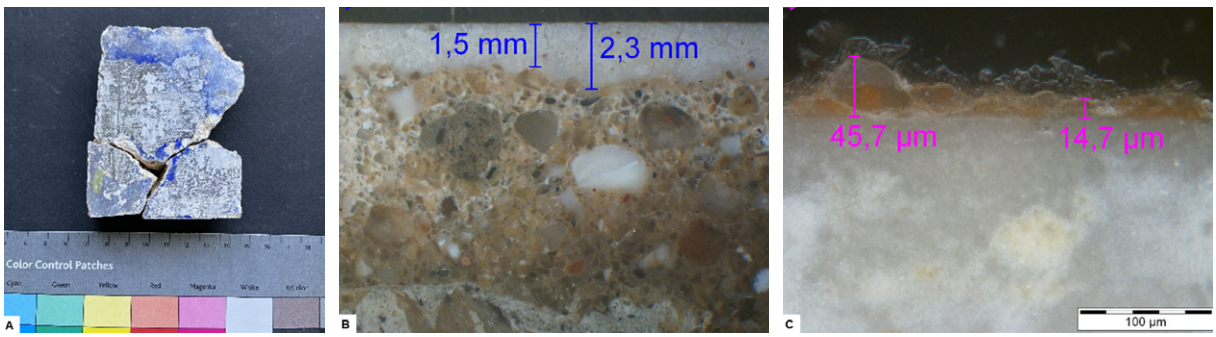

Figure 2. Sample collected from the north façade of the Casa da Pesca showing a blue pigment (A); and stereozoom microscope images of a rendering mortar sample collected from the south-facing gutter wall with measurements of the stucco (B) and finishing paint layer (C) thicknesses

3.2 Macrostructural characterisation

The main mechanical and physical results indicate that the original rendering mortars are cohesive and compact, exhibiting mechanical performance typical of high-quality lime mortars (compressive strength ranging from 1.5 MPa to 3 MPa and moderate to low water capillarity coefficients). These characteristics align with the composition, with traces rich in lime and well-graded sand. However, contrary to what would be expected, the presence of a finishing layer of lime (stucco) in some samples leads to more variable mechanical performance and, in general, a slight increase in the capillarity coefficient. This performance suggests the presence of micro-cracking, which may cause a loss of mechanical properties and contribute to an increase in the rate of capillary absorption. Besides, the finer grain size distribution of the stucco may also increase the porosity and consequently enhance water absorption and reduce mechanical strength. Overall, despite some biological colonisation, all the original rendering mortars are in a good state of conservation, reflecting well-formulated and well-executed mortars.

4. Conclusions

The results showed that all the external surfaces of the Casa da Pesca renders are composed with mortars consisting of two layers of calcium aerial lime with siliceous and carbonate aggregates. The mineralogical composition reflects the use of locally sourced materials. It appears that the internal layers have a higher binder/aggregate ratio than the external layer. Moreover, the internal layer contains finer aggregate particles than the external layer, with the presence of clay materials, such as mica, kaolinite and hematite. In addition, all the collected samples taken from a height of
~ 1 m are covered by a thin stucco layer composed of calcium lime, which is painted with mineral pigments ranging in colour from red-ochre to yellow-ochre, with some ultramarine, blue pigment also found. These differences in stratigraphy may suggest previous retrofitting interventions in areas showing a degree of stucco degradation, or they could simply reflect the original composition, with the existence of a mural painting on an upper level.

Overall, the results lead to the conclusion that the mortars are mostly original and in very good condition, showing only superficial biological colonisation. Given the historical and artistic value of the existing mortars, their conservation and preservation are strongly recommended. As a conservation strategy, it is suggested to preserve the existing renders, removing only the layers that have experienced functional degradation. For new repair mortars, materials with the same compositional and aesthetic characteristics should be used, specifically calcium lime-based compositions similar to the existing ones. The paints applied should also be compatible, based on aerial lime and mineral pigments, to potentially facilitate the elimination of moisture from within the walls. The study provided some information on the pigments used; however the patterns should be further investigated.

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Assessing reusability of a bio-stabilized earthen plaster

1. Introduction

Earth-based plasters are traditionally produced by applying a mortar made by mixing an earth with water. If the earth is too clayish, supplementary sand-size aggregates (natural sand or recycled aggregates) or natural fibres resulting from agro-residues are frequently added to control drying shrinkage, so that they can fulfil the requirements for indoor coatings: presenting adequate workability and density to be easily applied, adhesion and mechanical strength to adhere well to the wall they protect and to be durable to indoor actions, without cracking to present good aesthetics. Furthermore, they should have high adsorption/desorption capacity to act as moisture buffers and contribute passively to energy efficiency and occupants' comfort and health[1]. Finally, to optimize their environmental impact, they should be reusable when reaching their end of life, just by crushing and mixing again with water. Therefore, they are highly ecological in comparison to plasters made with other mortars[2], as cement-based or other industrial binders.

However, sometimes low contents of other materials are added to earth mortars formulation to provide higher resistance to water that can have accidental contact with the plaster, for instance when a window is left opened when it rains or when the floor is cleaned with water. Those additions can be bio-based, such as vegetal fibers and oils[3], cow dung (cut fibers and biocompounds resulting from cow digestion)[4] and other types. But sometimes mineral reactive materials can be also added, namely binders such as hemihydrated calcium sulfate[5], air lime[6] or natural hydraulic lime[7].

Nowadays, the addition to earth-based mortars of low embodied energy non-chemically reactive materials is much encouraged, both as supplementary aggregates or fibres, instead of natural sand, and as stabilizers, namely within RILEM TC BEC and the DIN standard for earth plasters1. As the use of cow dung has long tradition on many societies worldwide, this study assesses the effect of this addition on an earth plaster and the possibility of its reusability.

2. Experimental campaign and results

A reference mortar was produced with 1 volume of an earth from metropolitan region of Lisbon, in Caparica (labelled CAP earth), adding 1.5 volume of natural sand. To evaluate the cow dung (CD) effects a volumetric proportion of 20% of CD (calculated based on the total volume of the dry components: CAP earth plus added sand) was added. The CD was freshly collected on Moita, Portugal, and was added after

1 DIN 18947 2024.
2 Santos et al. 2021.
3 Lima et al. 2016.
4 Pachamama et al. 2024a.
5 Santos et al. 2024.
6 Santos et al. 2017a.
7 Santos et al. 2017b.

being composted for 7 days to eliminate possible biological contaminants. Further details on the earthen mortar materials can be accessed elsewhere[8].
The mortars were mixed with water and standard prismatic samples 40 x 40 x 160 mm3 and 50 x 40 x 20 cm3 plaster samples were produced, the latter applied on both adobe and hollow ceramic brick masonries. After hardening and drying for 30 days, to access the reusability, part of the prismatic CD added earth mortars were crushed and mixed again with the same content of water used previously, producing a second life mortar and samples, which were left to dry for 30 more days. The reference mortar (CAP-REF) and both the original and the second life samples with CD addition were tested for linear shrinkage, density, water resistance by immersion, adhesive, compressive and flexural strengths. Results are presented in Table 1 and Figure 1. They show that the CD addition: limits shrinkage, what minimizes cracks appearing; reduces the mortar density, facilitating application and increasing adhesion; do not significantly affects the mechanical strength; expressively increase the water resistance. The reused mortar with CD shows similar behaviour, but reduces a little less linear shrinkage and mortar density; reduces less than 10% the mechanical strength; still increases the adhesive strength, even less expressively; keeps the contribution to improve water resistance.

Earth mortars	Linear Shrinkage (%)		Dry bulk density (g/cm³)		Compressive Strength (MPa)		Flexural Strength (MPa)		Adhesion adobe (MPa)		Adhesion brick (MPa)	
	Average	Dev.	Average	Dev.	Average	Dev.	Average	Dev.	Average	Dev.	Average	Dev.
CAP-REF	1,56	0,03	1,69	0,01	1,25	0,04	0,53	0,02	0,13	0,01	0,06	0,01
CAP-REF +20CD	1,14	0,04	1,47	0,02	1,20	0,01	0,57	0,02	0,16	0,01	0,09	0,00
REUSED	1,24	0,03	1,55	0,01	1,06	0,05	0,51	0,02	0,14	0,01	0,07	0,01

Table 1. Linear shrinkage, density, compressive and flexural strength, adhesion on adobe and brick masonries of mortars

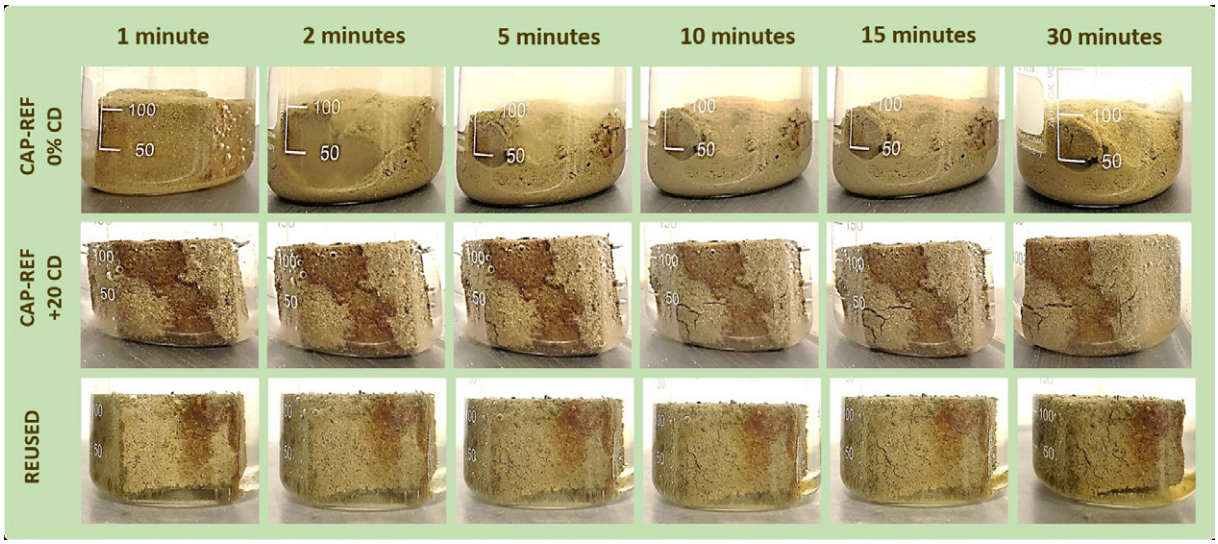

Figure 1. Immersion in water test for up to 30 min: from top to bottom, CAP-REF mortar and mortars with 20% of CD addition, both original and reused.

8 Pachamama et al. 2024b.

3. Final remarks

This study shows that the addition of cow dung does not compromise the reusability of the studied earthen mortar, although the effect of the addition is reduced when testing the second life mortar in comparison to the original. The effect of other bio-based additions and chemically reactive ones should also be studied. Contrary to cow dung, it is expected that the addition of chemically reactive binders, turning the earthen mortar an artificial stone, compromise their reusability.

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Preliminary Analysis of Lime Plaster used in the Syquia Mansion, Vigan, Philippines

1. Introduction

On July 27, 2022, a magnitude 7.0 earthquake struck northern Philippines, severely affecting the Historical Center of Vigan City, a UNESCO World Heritage site[1]. Among the heavily damaged structures was the Syquia Mansion, a 19th century vernacular house that now serves as a museum, displaying paintings, furniture, and offering a glimpse into the life of an upper-class family during the Spanish Colonial Period. As one of the oldest houses in Vigan, it exemplifies the traditional bahay na bato (literally, "stone house") architectural style, featuring a ground floor constructed of clay bricks, lime mortar, and stone, while the upper floor is made of wood. The destruction caused by natural disasters, such as earthquakes, highlighted the vulnerability of historical structures. Their subsequent restoration, however, needs to adhere to established conservation principles, including material compatibility, minimal intervention, and reversibility, ensuring their preservation at the same time.

2. Materials and Methods

To ensure compatibility of materials during the restoration process of the Syquia Mansion, the characterization study of its original plaster was conducted (see Figure 1). The plaster sample was collected from one of the walls, designated as Wall 3, located on the second floor of the mansion (Figure 1A). The primary function of the plaster was both decorative and protective, serving as a barrier against moisture originating from within the wall. A single sample from Wall 3 was subjected to characterization. Notably, Wall 3 remained in its original, preserved state, unlike the other walls, which have already undergone restoration.

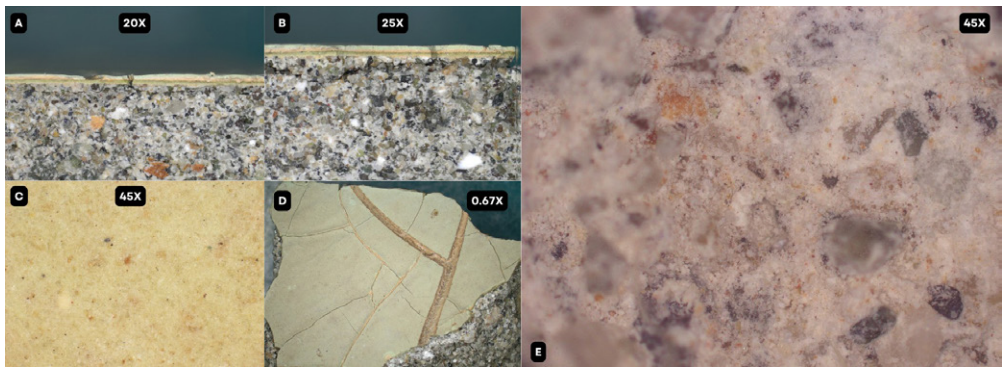

Figure 1. Microscopy images of the plaster sample from Syquia Mansion at different magnifications. (a) Cross-section showing all layers (20x). (b) Cross-section with higher magnification (25x). (c) Surface view (45x). (d) Plaster sample slightly tilted (0.67x). (e) Aggregates embedded in the lime matrix (45x).

1 Philippine Institute of Volcanology and Seismology 2022.

Various analytical techniques were employed, including Fourier Transform Infrared Spectroscopy (FTIR), Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), and X-ray Fluorescence (XRF), to assess its composition and properties.

3. Results and Discussion

FTIR, XRF, and XRD analyses indicated that the plaster is primarily composed of silica- and calcium-based minerals, consistent with the presence of lime mortar and sand. DTA results confirmed its hydraulic nature, with a CO_2/H_2O ratio of 3.2, which suggests hardening in the presence of pozzolanic materials[2] . TGA analysis revealed significant weight loss between 700°C and 850°C, characteristic of $CaCO_3$ decomposition and CO_2 release. FTIR spectra exhibited distinct carbonate ion (C-O) peaks at 713 cm^{-1}, 873 cm^{-1}, and 1407 cm^{-1}, while a broad peak at 1000 cm^{-1} indicated the presence of quartz (Si-O)[3]. Cross sectional image (Figure 1B) shows multiple layers, suggesting that the surface is composed of lime water. XRF analysis showed the relationship between silica and calcium oxide content is approximately 1:1 ratio. These findings indicate a low silica content relative to standard lime mortars, reinforcing the hypothesis that the surface plaster consists of lime water instead of the conventional lime mortar. XRD analysis also identified the silica mineral tridymite, which is formed above 870°C[4].

4. Conclusion

Experimental results showed that for restoration, the recommended surface plaster should be hydraulic lime water, and the firing temperature during the production process should be greater than 870°C. Pozzolanic materials should also be added with the limestone raw material during firing.

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Characterization of Finishing Plasters in Monumental Terracruda Sculpture: Case Studies from Buddhist Archaeological Sites of Kara Tepe (Uzbekistan) and Tepe Narenj and Qol-e-Tut (Afghanistan)

1. Introduction

1.1 Aim of research

This study is part of a multidisciplinary research project dedicated to the technological analysis of Buddhist monumental terracruda sculptures (unfired clay, as opposed to terracotta) for conservation purposes. By integrating diagnostic investigations on selected examples from Central Asia and Afghanistan with insights from historical texts and ethnographic research, the project seeks to elucidate the complex manufacturing process behind these multi-material artifacts. In this contribution, we present our characterization of the materials used to create the distinctive finishing plasters for the polychromies of these sculptures.

1.2 Monumental Terracruda Sculpture

Monumental terracruda sculptures are typically large-scale works made primarily from unfired or air-dried clay. They are always integrated into their architectural or environmental context and rely on an internal core—commonly composed of wood, stone, or bricks—for structural stability. The modeling pastes are applied in successive layers, with carefully controlled drying periods between applications. This sculptural method emerged in Central Asia around the 2nd century BC and, following the spread of Buddhism along the Silk Roads, gradually reached East Asia and the Himalayas, where it has continued to be practiced to the present day[1].

1.3 Hypothesys of research

Drawing on sacred literature and traditional knowledge documentation, several questions have emerged regarding the preparation and material composition of finishing plasters used to support polychromy. When white, what materials were employed? If calcium sulphate was used, was it in its hemihydrated or dihydrated form? Was fibrous material incorporated? Were organic binders systematically added? Addressing these questions is crucial for understanding the pictorial techniques that enabled polychromy in these sculptures, informing more targeted conservation interventions, and evaluating their historical and artistic implications in terms of dissemination.

2. Materials & Methods

Archaeological examples from Buddhist sites—including Kara Tepe (2nd–4th centuries CE, Uzbekistan), Tepe Narenj (5th–10th centuries CE, Afghanistan), and Qol-e-Tut (5th–11th centuries CE, Afghanistan)—have been analyzed using a wide range of diagnostic techniques. Petrographic and mineralogical studies have been conducted to examine the manufacturing process and mineralogical composition of the

1 López-Prat et al. 2024b.

Figure 1. Body and head of a monumental terracruda Buddha from Qol-e-Tut (Kabul, Afghanistan)

finishing plasters and polychromies[2], while the presence of fibrous material has been assessed through microscopic techniques, as well as phytolith and fiber analyses[3]. Additionally, epifluorescence, FTIR, GC-MS, and omics methods have been employed to identify organic binders incorporated into the plasters[4].

3. Conclusion

The results suggest a distinctive sculptural tradition in the preparation of finishing plasters, where white minerals were crushed and placed on top of clay-based modeling pastes to support polychromy. When calcium suphate-based plasters were employed, they were applied in their dihydrated form and mixed with gluing agents. This systematic use of inorganic and organic binders, coupled with the consistent incorporation of fibrous materials, reflects a well-established technological practice in the creation of monumental terracruda sculptures.

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Hygroscopic performance of vernacular earthen coatings of Santiago, Chile

1. Introduction

Earthen plasters are recognized by their ability for improving the hygrometric conditions of indoor spaces through their moisture sorption and desorption properties[1]. However, this type of plasters is often composed of a set of layers where different materials can be combined, especially in vernacular systems. Some of these layers may either keep the hygroscopic features of earthen mortars or may hinder and reduce their sorption/desorption capacity. It is, therefore, pertinent to analyse the influence of different finishing layers of earthen coatings and, for old plasters, the effect of several finishing layers overlapped over time.

This study is part of an ongoing PhD research of the first author on the characterization of vernacular earthen coatings of earthen buildings from Chile. These traditional coatings are characterized by a well-defined system of three main coats, from the wall substrate to the visible surface layer: a thick and cohesive scratch coat made of earth and vegetal fibres, a sandy friable base coat, and a set of different finishings[2]. The latter depends on the function, on the type of finishing surface intended, on economic reasons, and on whether it is for rendering (exterior) or plastering (interior). In some case studies, the finishing is composed by a set of layers resulting from successive renovations which sometimes represent different periods of the building. These finishing materials, in addition to decorating the wall, should contribute to the protection and conservation of the earthen heritage walls they coat .

In addition to the results here presented, other tests are being carried out to evaluate the material characterization and performance of the coatings.

2. Methodology

To accomplish the objective of comparing sorption properties of different vernacular coatings from Santiago, some samples were extracted from selected case study walls with all the layers composing these plastering systems, from the substrate to the surface. For comparison, a rendering system was also included. The case study MSJJVV_02 is from a central neighbourhood vernacular building, made with adobe masonry-filled timber frame walls. The case studies SCC10_02 and SCC10_03A are taken from an adobe outbuilding of an important building, also in adobe masonry, located in main centre of Santiago. SCC10_02 represents the only exterior sample of the four case studies. Finally, SCC10_04 samples were taken from the interior surface of the adobe façade of this building, named Casa de los 10. All samples present the two aforementioned layers of earthen mortar.

To proceed to the sorption/desorption test, the extracted samples were divided in 6 specimens that were than prepared applying adhesion aluminium tape (3M Scotch) to the back and the sides. The finishing remained exposed in 3 samples and was removed in other 3; in that case, the sandy earth layer remained

1 Röhlen, Ziegert 2013.
2 Marchante, Rivera 2023.

exposed. The test was performed based on the DIN 18947[3] and Lima et al.[4]. The samples were stabilized at 50% relative humidity (RH), presenting constant mass 24 h before running the test. The climatic chamber was then set at 80% RH and 23 °C. The sorption cycle was extended to 24 h, and a 24 h desorption cycle set at 50% RH and 23 °C was also included.

3. Results and Discussion

In Figure 1, the results of the samples with and without finishing revealed significant differences in all of them, except for the SCC10_02 sample set (the only render, with a rain-washed gypsum-water-based paint finish in degraded conditions), where the difference was minimal. The greatest difference was found in the MSJJVV_02 case study, with sorption results, after 24 h, 3.26 times higher in the samples without the finishing. This case study finishing layer has a first gypsum layer with two different water-based paintings, and finally a glued wallpaper. It has the lowest sorption of all the four case studies with finishings, followed by SCC10_04 and SCC10_03A. The first of these two has a lime-based layer and a vinyl paint on top, and the second a lime or gypsum-based layer and vinyl or acrylic paint finishing. Comparing to

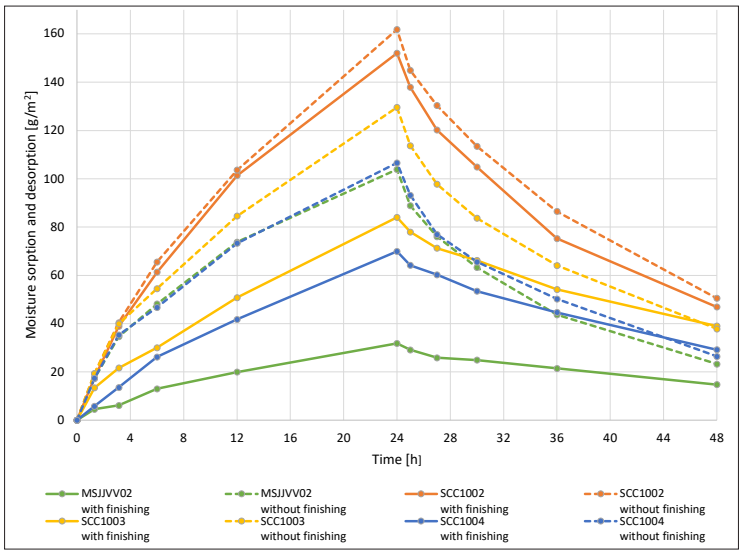

Figure 1. Left to right: sorption/desorption curve of the four case studies, with and without finishings; detail of the finishings, moisture content (MC) after 24h sorption and remaining MC after desorption and the ratio of both sorption without and with finishing for each case study

Case study	MSJJVV02	SCC1002	SCC1003A	SCC1004
With finishing	1.Lime mortar and limewash (blue) 2.Gypsum-water-based paint (green) 3.Limewash (blue) 4. Gypsum-based paste with vinyl binder (ochre) 5. Glued wallpaper	1.Degraded limewash or gypsum-water-based paint	1. Thin lime or gypsum mortar 2. Acrycilic or vynil paint (ochre)	1. Lime mortar 2. Acrycilic or vynil paint (yellow)
24h sorption [g/m²]	31.9	152.0	84.0	70.0
Remaining MC [g/m²]	14.8	46.9	39.0	29.2
Without finishing				
24h sorption [g/m²]	103.9	161.8	129.6	106.6
Remaining MC [g/m²]	23.3	50.5	37.8	26.4
Δ 24h sorption without / with finishing	3.3	1.1	1.5	1.5

3 DIN 18947 2024
4 Lima et al. 2024.

sorption assessed on the same conditions on other earthen mortars[5-6], the sorption reached by the four case studies of vernacular coatings (composed by two earthen layers) without finishings, are higher. However, any of the systems released all the sorbed moisture.

4. Conclusion

Although the sorption capacity of plasters is very important for the contribution they may have to comfort and occupants' health, results have shown that finishing materials have a great influence on the sorption of the tested coating systems, being a reduction factor on their moisture buffering. The type of the finishing materials is of great importance determining this reduction factor. As along the life of the tested coatings several layers have been applied on top of each other, the results are not conclusive as to which layer and material is more prominent on reducing the sorption. The degraded limewash of SCC10_02 shows little impact on the hygroscopic behaviour of the system, contrary to the multiple finishes of lime and gypsum-based layers with glued wall paper of MSJJVV_02 case study.

Other tests are being carried out with specimens with a known single finishing to complement the results and conclusions. Along with these, other complementary hygroscopic tests are being performed, such as moisture buffering value and the determination of the water vapour permeability. These should provide more information about the hygroscopic properties and the hysteresis phenomenon in sorption/desorption cycles of earthen coatings.

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5 Santos et al. 2020.
6 Ranesi et al. 2021.

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Roman Cement: A Material to Preserve and to Conserve. Historical Production, Processing and Application in the Restoration of a 19th-Century Natural Binder

1. Introduction

It is well known that this hydraulic binder was invented in England, and thereit is general agreement in attributingagreed that Joseph Parker was granted the manufacturing patent (1796) to Joseph Parker.). It is also known that Roman Cement "'was obtained by firing calcareous marls at approximatelyabout 800-950°C in the areas surrounding London"limestone marls outcropping around London' [1] and that it became "'an important building material in Europeon the [European] continent and in the United States from, [starting] in the second half of the 19th century"century' [2]. It is estimated that "in Centralcentral Europe during the 18th19th century, "the majority of buildings were constitutedconstructed of Roman Cement, with peaks of 80 percent% in the cities of the Austro-Hungarian Empire" [3], demonstrating the successfortune and technological versatility of this 'lithocement,'"litho-cement", which today deserves properdue recognition forin terms of its historical significance. In the 20th century, its use rapidly declined rapidly in favorfavour of Portland cements.cement. However, the performance aspect of Roman Cement is undeniable. Unlike Portland, it has stood the test of time, proving, among other things, to be akin to and compatible with the physical and mechanical characteristics of the traditional materials of 19th-century buildings (bricks, natural stones), often used in combination with this binder.

Several studies have been conductedundertaken on this type of natural cement, of which we would like to mention the projects RENDEC (1997-1999) [4], ROCEM (2002-2007), later merged into ROCARE (2007-2012) [2],] projects, which are definitely significant regarding the classification of raw materials and mineralogical composition of Roman Cement. However, they focusthese studies focused on natural cements producedthe analysis and tracing of buildings located in England, France, and Centralcentral and continental Europe, without specifically mentioning the Italian case.

This research, carried out as part of a broader doctoral project, aims to fill this gap by investigating the spread and use of Roman Cement in Italy, particularly as a binder in historic public and private architecture.

Although Roman Cement has now been replaced by modern cements, according to the sources cited in the bibliography, it boasts excellent strength, and durability, as well as compatibility with traditional materials used in architecture, and a recognized aesthetic value.

For this reason, one of the outlined objectives is to encourage the future use of Roman Cement as binder to be used in the preparation of intervention mortars for the restoration of historic buildings. This will require verifying the chemical-physical compatibility of such mortars with a wide range of mortars and natural stones present in the Cultural Heritage, as well as an analysis of the properties that it shows when mixed, in different percentages, with the binders traditionally used in restoration interventions.

It is well known, however, that the spread of Roman Cement involved a few centres in northern Italy; the best known case is that of Turin, where there are several buildings in which natural cement was used as a binder, and its use in important examples - such as the Castello del Valentino, or the Mole Antonelliana, to mention a few - was also favoured by its proximity to the major Roman Cement production centres: those near Grenoble (France).

A new architectural complex is added to the list, the Palace of the Anatomical Institutes in Turin, which houses several departments of the University of Turin and three museums. Here, the diagnostic analyses preparatory to the restoration work revealed the presence of Roman Cement in the plaster coverings, a presence that is not surprising due to both the age of construction and the geographical context. Taking this aspect into account, the project for the conservation work on the Palace included the addition of Roman Cement in the mortar mix to fill in the gaps in the plasterwork, with the intention of pursuing a respectful and consistent approach with the original materials, also with a view to maximum compatibility, both material and historical.
But the binder's fields of use are not limited to integrative restoration: exploiting its rapid setting and hardening, Roman Cement is also well suited for emergency interventions, moreover in adverse conditions such as the underwater and saline environments of the Venice lagoon.
A material, therefore, with excellent properties of hydraulicity, resistance and durability, all to be discovered or, better, rediscovered.

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Tracing Scagliola's Secrets: Material Analysis of Marble Imitating Interiors from 1770-1810

The specialized technique of gypsum-based stone imitation, known as scagliola, remains an underexplored area in the study of architectural surfaces and interiors. Developed around 1600, scagliola gained widespread use across Central Europe from around 1700 until the outbreak of the First World War. However, despite its historical significance, only a limited number of material-specific studies have examined this technique in depth[1].

As part of a doctoral thesis, key technical and material advancements in scagliola applications in Vienna were identified and investigated[2]. During this work further questions emerged regarding the extent to which the executed plasterwork aligns with written records from 1770 to 1810, as well as potential regional or cross-border variations in its implementation. To investigate these aspects, samples were taken from the technological collection of the Federal Monuments Authority Austria (Figure 1) and analysed in relation to previously studied scagliola surfaces from different rooms (1770) in the Schönbrunn Castle and the Auersperg Palace (1802) in Vienna. Two of the newly taken samples originate from Lower Austria, near Vienna, dated around 1780 while another, dating to around 1810, is attributed to a 'Prussian' castle in Berlin[3]. The latter was included as a comparative example for this period.

Figure 1. Scagliola fragments in the technological collection of the Federal Monuments Authority Austria

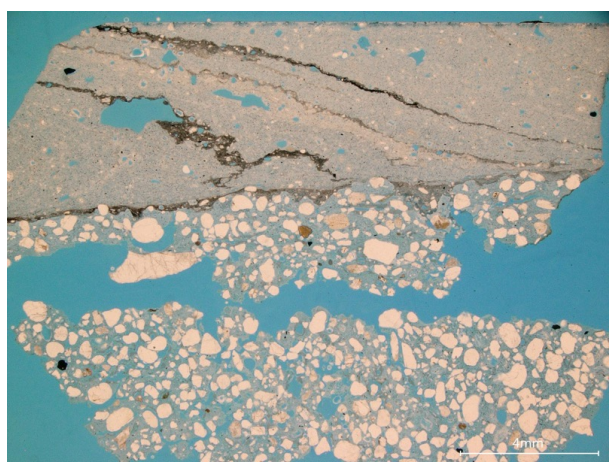

Figure 2. Thin section micrograph of a gypsum-based plaster with silica sand (bottom) and scagliola layer (top) dated around 1810 (plane-polarized light)

1 Wittenburg 1999; Freire et al. 2016; Freire et al. 2020; Fuchs, Pintér 2022.
2 Fuchs 2024, 29-35.
3 Within the technological collection the labelling of this sample (TS89) mentions 'aus einem preußischen Schloss in Berlin' (translated 'from a Prussian palace in Berlin').

1. Analytical Methods

To assess the material used and the manufacturing process, six samples were examined and compared, all of which were chronologically dated between 1770 and 1810 using macroscopic observations and photographic documentation. The samples were embedded in blue-dyed epoxy resin and prepared as polished thin sections for detailed study. Initial observations were conducted using a digital microscope (Keyence VHX-6000), while further detailed analyses were performed with a polarized light microscope (Olympus BX-40) in both plane- and cross-polarized light. Fine-grained, binder-related components were further examined with a scanning electron microscope (JEOL JSM-IT200) in low-vacuum mode. This combination of methodologies provided a comprehensive understanding of the composition, structure, and damage behaviour of the scagliola.

2. Material Composition and Variations

Scagliola interiors in Vienna were historically applied directly to the wall surface until around 1900. Therefore, examining the underlying plaster is essential for dating and determining the original structure, which proved to be a key characteristic in the interiors[4]. Beyond the composition of the binding agentbinder, the aggregates usedalso provide valuable insights into the sourcing of raw materials and can contribute to the dating of previously undocumented fragments. Many Viennese scagliola surfaces created up to the mid-18th century - and in some cases even into the second half of the century - were applied to a (dolomitic) lime plaster. However, in 1772, Sprengel recommended the use of a gypsum-lime mortar as a substrate[5], coinciding with the intensification of gypsum quarrying in Lower-Austria southwest of Vienna[6]. This raises the question of how written recommendations influenced practical applications. Despite the accessibility of raw materials, an analysis of two samples from Schönbrunn Palace - the Maschinenzimmer and the Rosa Zimmer[7]- revealed a lime-based substructure with a layer thickness of approximately 4 mm. The plaster from Sierndorf Castle, dating to around 1780, consisted of a lean, porous lime-based mix containing carbonate and silica grains exhibiting an abraded surface. In contrast, the scagliola layer at the Parish Church in Karnabrunn (around 1780), was based on a gypsum-lime mix that included carbonate and glauconitic sand, most likely sourced from the Molasse zone west of Vienna. Its surface exhibited irregularities, a calcium carbonate precipitation layer and gypsum particles as residues and/or recrystallized particles in secondary air voids measuring between 0.2 and 0.3 mm. These later components indicate the average grinding fineness of the gypsum before mixing it with water. By 1810, a transition to pure gypsum plaster became evident in samples from the Rosenkavaliersaal in Palais Auersperg and a Prussian palace. In this type of plaster, no added lime was detected and the aggregate used was a well-rounded fluvial sand of silicate origin. It was likely mixed dry with pigments such as red ochre, following the so-called Italian method, which is recognizable by its parallel structure (Figure 2). The production process resulted in irregular yet systematically aligned pores, indicating the possible use of an adhesion promoter, which would not typically be necessary for gypsum plaster. Optical and chemical characteristics of the identified binder-related particlesphases indicate that the calcium sulphate raw material was fired at low temperatures (<200°C), the presumable). The presence of fibrous anhydrite IIIII crystals in some samples, however, may indicate hot spots (200–300°C) during the calcination.

3. Conclusions

The study provides insights into the evolution of scagliola plastering techniques in Vienna, emphasizing the transition from lime-based to gypsum-based substrates. The role of raw material availability, written

4 Early scagliola intarsia interiors, such as the decorations at the Munich Residence in the early 17th century, were applied on a wooden support, which allowed the later removal.
5 Sprengel 1772, 234-235.
6 Otruba 1987, 172.
7 Archive of the Federal Monuments Authority Austria, Scientific Laboratory; GZ: BDA-14800.obj/0004-WIEN/2019, Nr. 150/19 – 151/19.

recommendations, and practical applications all contributed to these developments. Moreover, detailed scientific analysis helps identify material compositions and secondary influences, providing valuable insights for tracing historical techniques and for upcoming conservation efforts.

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Scagliola in the interiors of Baroque palaces and churches in Czechia – material investigation

1. Introduction

The imitation of marble can be achieved with different materials and techniques[1-2-3-4]: scagliola, stucco lustro, marmorino, marezzo, etc. Recently, the artificial marble in scagliola (or stucco marble) technique applied to baroque altars throughout the Czech Republic started to be investigated. Ten samples were collected from various locations, including palaces, churches, and monasteries, representing diverse artistic and historical contexts. Samples generally consist of a superficial layer of artificial marble, occasionally overlaying a support plaster. The objective was to determine the chemical and mineralogical composition of the artificial marble and underlying mortars, providing insights into the materials and techniques used during the Baroque period. The analysis included optical microscopy for stratigraphy and microstructure assessment, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) for detailed insight into the fine-grained composition, micro-Raman spectroscopy (pigment characterisation), and thermal gravimetric analysis (TGA/MS) for the characterisation of the binder.

2. Summary of results

The artificial marble samples consisted mainly of gypsum ($CaSO_4 \cdot 2H_2O$) as the primary binding agent. SEM/EDX analysis revealed the presence of minor mineral phases within the gypsum matrix, including quartz, feldspar, calcite, and celestine ($SrSO_4$). Micro-Raman spectroscopy revealed a complex palette of pigments used to achieve the desired colours and effects, including indigo, goethite (α-$Fe^{3+}O(OH)$), hematite (Fe_2O_3), carbon black, lazurite (ultramarine), pyrite (FeS_2), and rutile (TiO_2). The underlying mortars were composed of moderately hydraulic lime as the binder and sand as the aggregate. The sand consisted primarily of quartz and feldspar grains, with minor amounts of mica. Relicts of clinker minerals were observed within the hydraulic lime binder, indicating its origin. The thermal analysis (TGA) of the samples confirmed the presence of gypsum as the main component, with a significant dehydration event occurring between 100 and 200°C. A mass loss observed in the range of 200 and 550°C suggested the presence of organic matter within the samples (app. 1-2 wt.%). Evolved gases analysis by mass spectrometry detects in this thermal interval fragments of organic additive, which was usually animal glue1 (Figure 2). A minor endothermic event from 600 to 800°C indicated the decomposition of calcium carbonate. Table 1 summarises the calculated gypsum and calcium carbonate content in particular samples.

The stratigraphy of the samples, as observed under a binocular microscope (Figure 1), revealed distinct layers of artificial marble and underlying mortar suggesting a deliberate layering technique reflective of the original decorative intent and subsequent restoration interventions. The artificial marble layers varied in thickness and colour, depending on the pigments used. The underlying mortar layers were typically

1 Fuchs, Krist 2020.
2 Reithmeir 2024.
3 Zuena M., Fondi V., Adembri 2022.
4 Wedekind 2010.

sample	weight loss (wt.%)			content (wt.%)	
	gypsum dehydration	organic compound combustion	calcium carbonate decomposition		
	70-200°C	200-550°C	550-750°C	$CaSO_4.2H_2O$	$CaCO_3$
Prague, Pachta Palace	18,5	0,9	1	88,1	2,3
Prague, MacNeven Palace	19,4	1,1	0,7	92,4	1,6
Hradčovice	18,8	1,9	3,2	89,5	7,3
Rajhrad	17,8	1,2	2,9	84,8	6,6
České Budějovice	18,4	1,9	1,3	87,6	3
Litoměřice	18,3	2	0,5	87,1	1,1
Štípa	18,5	2,3	0,3	88,1	0,7
REF $CaSO_4.2H_2O$	16,1	0,7	3,7	76,7	8,4

Table 1. Gypsum and calcium carbonate content as detected by TGA/DSC.

Figure 1. Photograph of artificial marble from the monastery in Rajhrad (left) and Štípa (right).

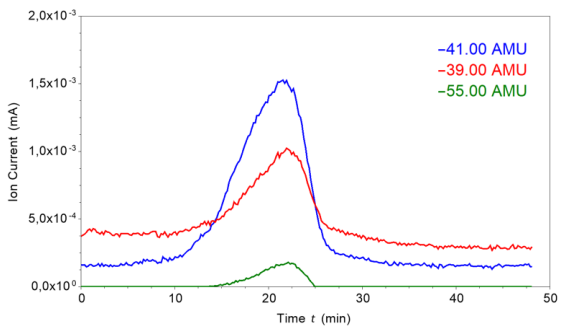

Figure 2. Detection of organic matter fragments during thermal analysis by mass spectrometry.

light brown to sandy in colour and exhibited a coarser texture compared to the artificial marble. SEM/EDX elemental mapping provided detailed insights into the fine-grained composition, revealing the presence of calcium sulfate dihydrate along with accessory minerals such as quartz and celestine.

Conclusions

The multi-analytical approach has provided a detailed understanding of the chemical and mineralogical properties of gypsum-based plaster used in baroque altars. The observed variations in microstructure and pigment composition are linked to the original production techniques and later conservation treatments. These findings enhance our understanding of historical decorative practices and offer valuable insights for future restoration efforts. Further studies are recommended to integrate these results with historical documentation for more targeted conservation strategies.

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Material characterization of traditional Moroccan Tadelakt: an an experimental archaeometric approach to an ancient lime-based plaster

1. Introduction

Tadelakt is a traditional Moroccan plastering technique involving the use of lime (Figure 1)1. It has historically been used to decorate and waterproof cisterns, hammams, fountains and interior surfaces. Its distinctive properties — water repellency, antibacterial effects, and a smooth, polished appearance — result from a meticulous process involving the application of special lime, compaction with river pebbles, and surface treatment with natural black olive soap. Despite its increasing use in contemporary sustainable architecture, little scientific data exists on the properties of Marrakech lime or the chemical transformations that occur during the tadelakt process2. This study takes an experimental archaeometric approach to investigating the mineralogical, microstructural and chemical properties of the raw materials and finished plaster.

Figure 1. Application of Tadelakt plaster

Figure 2. Traditional lime kilns of Marrakech lime

2. Methods and Materials

A multi-analytical experimental approach was adopted. to characterise the material properties of Tadelakt. The study analyzedanalysed limestone samples from Marrakesh quarries and Tadelakt plaster specimens prepared using traditional artisanal methodstechniques.

The following techniques were employed:

- Petrographic analysis (thin sections) to examine the texture, microstructure, and diagenetic features of both the raw limestone and the plaster;
- X-ray diffraction (XRD) to determine the mineralogical composition of the calcined lime and the set

plaster;
- Scanning Electron Microscopyelectron microscopy (SEM) for high-resolution imaging of the microstructure and reaction products;
- Fourier-Transform Infrared Spectroscopy (FT-IRtransform infrared spectroscopy (FTIR) on the soap-treated surface to assess the chemical interactions between calcium hydroxide and the fatty acids in black olive soap;
- Cathodoluminescence (CL) imaging to investigate the diagenesis of the original rock;
- Physical and mechanical tests, including compressive strength and capillary water absorption;
- Contact angle measurements were used to quantify surface hydrophobicity;
- Water vaporvapour permeability tests were performed to assess breathability and compatibility with architectural applications;
- All samples were prepared in collaboration with artisans using traditional application and polishing techniques.

3. Preliminary results

Petrographic analysis and XRD results confirmed that the Marrakech limestone is fine-grained and predominantly micritic with a low fossil content and minimal impurities. This makes it suitable for producing high-quality lime.
SEM-EDS elemental analysis and mapping revealed a non-homogeneous microstructure, as well as a pozzolanic reaction between the silica components and the calcitic part. Contact angle measurements corroborated these findings, revealing that the treated surfaces exhibited significantly higher contact angles with water, indicating enhanced water repellency. Mechanical and physical tests showed moderate compressive strength, which is consistent with that of finishing plasters, as well as high hardness and adhesion to the substrate. CL imaging, FT-IR analysis and vapour permeability measurements are ongoing.

4. Discussion and conclusion

This research provides the first integrated mineralogical, chemical and physical characterisation of Tadelakt, focusing on Marrakech lime and its processing throughusing artisanal practices. The combination oftechniques. Combining CL, FT-IR, SEM and XRD analyses revealed the fundamental role ofthat carbonate composition, surface treatments and material processing play a fundamental role in defining thedetermining Tadelakt's properties of Tadelakt. Despite the fact that the original limestone was not being fired completely homogeneously due to the use of traditional lime kilns (see Figure 2), this did not affect the material's excellent properties of the material. Preliminar. Preliminary physical and mechanical tests demonstrated the material's goodhigh performance and highexcellent water repellency. The low environmental impact and durability of Tadelakt make it a valuable technique forin contemporary construction, combining heritage materials with modern, sustainable design strategies.
This study has provided new insights into the scientific principles behind the Tadelakt technique by using an experimental archaeometric approach to relaterelating material properties, traditional processing methods and functional performance using an experimental archaeometric approach.

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Field evaluation of the properties of injectable grout and repair plaster for the stabilisation of 17th c. painted gypsum-wood coved suspended ceiling

This study focuses on the stabilization treatment developed for a 1657 painting of Michel Corneille l'Ancien on gypsum-wooden ceiling decorating the Galérie de Psyché in Hôtel des Ambassadeurs de Hollande, Paris, France. Characterization of the original materials was conducted using optical microscopy (OM), scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS), X-ray diffractometry (XRD), and Fourier transform infrared spectroscopy (FTIR) . Results shortlisted the selection of conservation materials, including gypsum, lime putty, marble dust, quartz and animal glue. Various mixes were tested and evaluated by simplified field tests based on established methods described in literature.

1. Painting and its substrate

1.1 Original technology

The suspended wooden laths appear to be splattered and embedded in a whitish plaster rich in long fibres. This is overlaid by a smoothly applied plaster of approximately 1-2cm thick. This plaster has high binder content, identified as gypsum with inclusions of quartz, calcite and charcoal. They seem to be intentionally incorporated. Some proteinic material was detected by FTIR and its presence is likely to delay the gypsum's rapid setting . Above this plaster, an orange-brown organic layer—possibly a sealant—is present, followed by the paint layer.

1.2 Conservation state

The painting exhibited long, deep cracks extending the entire ceiling, penetrating the full plaster thickness. Additionally, there were localized plaster losses, and detachments between plaster layers and the wooden laths (Figure 1). To address these issues, injectable grout was required to restore adhesion, along with plaster repairs to restore surface loss.

2. Treatment development and evaluation

The chemical and physical properties of treatment constituents should be compatible with the original materials while meeting the intervention criteria. Therefore, the treatments were designed to be gypsum-based. A no-additive plaster of Paris was selected as a binder due to its local abundancy and thus common use in plaster manufacture. However, its rapid setting time posed application challenges, prompting research into gypsum retarders, specifically lime putty and rabbit skin glue. For bulking, marble dust and quartz aggregates were explored. Tests were conducted on wood to stimulate the interface with the original material. The working and performance properties of the various mixes were qualitatively and comparatively evaluated both during application and after setting, applying bench tests onsite and in hidden areas in situ. To minimize any risk of hypothetic biological deterioration, all tests aimed to limit the amount of 3% rabbit skin glue (w/v).

2.1 Injectable grout

Performance and working properties were evaluated using the syringe, cup, drip, sandwich and in situ tests. Contrary to claims in the literature, lime putty showed no significant effect on prolonging the minutes-long gypsum setting time. In contrast, a 3% of animal glue used in a 1:4 (v/v) to dry materials (3 gypsum to 1 marble dust) and adding 1 (v) H2O for appropriate consistency, effectively extended the working time to approximately 5 hours, allowing for multiple injections and press installation. Reducing this amount of animal glue dispersion led to lower adhesion and shorter drying time. Amongst the various tested mixtures, this formulation demonstrated excellent injectability, good cohesion and adhesion, sufficient fluidity, adequate permeability, low water diffusion, and resistance to flexural and decompression tension.

2.2 Repair plaster

The plaster for fill losses was formulated using similar components to the injectable grout and assessed through a 5x6cm test plaster applications on wood and in situ. Two types were designed: thick plaster for deep losses, where extended drying time was unnecessary, and fine plaster for cracks and surface finishing, requiring slightly longer application time, adequate porosity and texture to support subsequent retouching with easy edge clearance.

The performance properties of the plasters were evaluated for cohesion, adhesion, porosity, and aesthetic integration, while key working properties—including application time, workability for modelling, and low water diffusion. The optimal repair plaster mix was gypsum/lime putty/marble dust 1:0.25:1 (v/v) and adding a small amount of 0.1ml of 3% animal glue and additional deionised water for a workable plaster giving a sufficient 30-minute working time window.

3. Conclusion

Field formulation of gypsum injection grouts and repair plasters and their evaluation have limitations and does not cover the tests for all the intervention criteria; however, they provide valuable insights into the behaviour of introduced materials. Additionally, this study demonstrates that even in small amounts, organic additives in gypsum can significantly alter the working and performance properties of the grout or plaster mix. Supplementary investigation into their long-term effects on deterioration and longevity would benefit both material science and conservation practice.

Figure 1. Detachment of the gypsum-based plaster from the wooden lath

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Exploring Gaji: Gypsum-Earth Plasters in Medieval Wall Painting Technology at Kolagiri, Dodorka, and Sabereebi Monasteries, David Gareji, Georgia

Abstract

Gaji — a naturally occurring gypsum-based rock—has been historically used in plasterwork across the Caucasus, Central Asia, and the Middle East[1]. However, its composition and properties vary significantly depending on geological source, quarrying practices, burning techniques, and application methods[2]. Despite its widespread historical use, gaji remains insufficiently studied, particularly in relation to medieval wall painting technologies[3].

The limited understanding of historic gypsum-earth plasters presents challenges in diagnosing deterioration phenomena and formulating effective conservation strategies. This study represents the first comprehensive investigation of plasters in three major medieval rock-cut monastery complexes in David Gareji, Georgia: Sabereebi, Dodorka, and Kolagiri[4]. These sites contain over ten painted churches, each featuring multilayered plasters and diverse decorative schemes dating from the 9th to 13th centuries.

Through a combination of archival research, field assessments, microscopic examination, and advanced material characterization techniques—including thin-section petrography, X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)—the study identifies plaster compositions, technological variations across time and geography, raw material provenance, and gaji production techniques. This research contributes new insights into the diversity of historic gypsum-earth plasters and supports future conservation efforts.

Figure 1. Remains of 12th–13th century wall paintings at Kolagiri Monastery, David Gareji, Georgia.

1 Mishmastnehi et al. 2025; Laue&Kleinmann 2018.
2 Tkeshelashvili 1979.
3 Sagaradze et al. 2023.
4 David Gareji Monasteries and Hermitage. https://whc.unesco.org/en/tentativelists/5224/. Accessed 04 April 2025.

David Gareji Monastery	Painting date	Number of plaster layers	Representative Fragments	Binocular image	Major composition	Investigation method
Sabereebi, Church V	The second half of IX	2 or 3 plaster layers	DG_Sab_V_F1		Gypsum, Anhydrate; Bassanite; Quartz; Plagioclase; Smectite; Kaolinite; Calcite; Weddelite + organic inclusions	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
			DG_Sab_V_F2		Gypsum; Anhydrate; Bassanite; Quartz; Plagioclase; Smectite; Illite; Kaolinite; Calcite; Weddelite	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
Sabereebi, Church VI	The second half of IX	Inner church has 1, 2 or 3 plaster layers; Outer church has 1 or 2 plaster layer, possibly with additional ground layer in some parts.	DG_Sab_VI_F1		Gypsum; Anhydrate; Bassanite; Quartz; K-feldspar; Plagioclase; Smectite; Illite; Kaolinite; Calcite; Weddelite	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
			DG_Sab_VI_F2		Composition: Gypsum; Anhydrate; Bassanite; Quartz; K-feldspar; Plagioclase; Smectite; Illite; Kaolinite; Calcite; Weddelite	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
			DG_Sab_VI_F4		Composition: Gypsum Gypsum; Anhydrate; Bassanite; Quartz; K-feldspar; Illite; Kaolinite; Calcite	In-situ and lab microscopy, XRD, ATR-FTIR
			DG_Sab_VI_F5		Gypsum; Anhydrate; Bassanite; Quartz; Smectite; Illite; Calcite	In-situ and lab microscopy, XRD, ATR-FTIR
Sabereebi, Church VII	The first half of X	2 or 3 plaster layers	DG_Sab_VII_F1		Gypsum; Anhydrate; Bassanite; Quartz; Plagioclase: Smectite; Kaolinite; Calcite; Weddelite; + organic inclusions (lower layer)	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
Sabereebi, Church VIII	The second half of X	**Inner church** has 1, 2 or 3 plaster layers; Outer church has 2 plasters	DG_Sab_VIII_F1		Composition: Gypsum; Anhydrate; Bassanite; Quartz; K-feldspar; Plagioclase; Smectite; Illite; Kaolinite; Calcite	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
Dodorka, Church of Christ	X and later undated	**Apse:** 1 or 2 plaster layers; **Burial niche** has 1, 2, 3 plasters	DG_Dod_Ch_F1		Gypsum; Anhydrate; Bassanite; Quartz; Illite; Calcite	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
Dodorka, Church of St. Demetrius of Thessaloniki	XII	2 or 3 plaster layers	DG_Dod_D_F1		Gypsum; Quartz; K-feldspar; Plagioclase; Smectite; Illite; Kaolinite; Calcite; Charcoal	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS
Kolagiri, Main Church	XII-XIII	2 or 3 plaster layers	DG_Kol_F1		Gypsum; Quartz; K-feldspar; Plagioclase; Smectite; Illite; Kaolinite; Calcite; Weddelite; Charcoal	In-situ and lab microscopy, XRD, ATR-FTIR, Thin-section, SEM-EDS

Table 1. Summary of the major composition of historic gaji – gypsum-earth plasters in monasteries researched within the David Gareji Complex

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Overview of Historic Mud Mortars in Diriyah, Saudi Arabia: from characterization to conservation

1. Historic Diriyah

Diriyah, situated along the Wadi Hanifah valley northwest of Riyadh, Kingdom of Saudi Arabia, was founded in the 15th century and served as the capital of the First Saudi State (1727–1818). Comprising multiple districts on plateaus overlooking the Wadi Hanifah oasis, Diriyah developed within an extensive defensive system. Ghasibah represents the oldest district, currently an undisturbed archaeological site. At-Turaif, established in 1766 as the royal administrative center, was inscribed on the UNESCO World Heritage List in 2010. Today, these sites are integrated within the Diriyah Gate development area, overseen by the Diriyah Gate Development Authority (DGDA). The Diriyah Foundation (DF) is specifically mandated to preserve and promote Diriyah's cultural heritage, acting as custodian of At-Turaif WHS,

Figure 1. At-Turaif World Heritage Site

Ghasibah, and over 100 other historical and archaeological assets, with dedicated conservation teams focused on their long-term preservation.

2. Assessment and analysis in multiple Diriyah sites

Traditional Najd architecture, characterized by a sustainable and climate-responsive design, finds its best expression in Diriyah. The historical development of this architecture is an exceptional expression of the resilience of the communities that adapted to live within a very harsh arid environment. Built with a mixed technology of stone and adobe, the various historical sites and assets show evidence of a continuous use of very peculiar patterns and construction techniques, including systems to increase the thermal performance and the use of natural ventilation, altogether combined with the maximization of the use of local resources.

To understand the characteristics of the original construction materials, their decay patterns, and to inform appropriate conservation strategies, since 2022 the DF conservation teams have conducted extensive campaigns of analysis across multiple sites. This paper presents findings focused on the most historically significant and authentic areas: Ghasibah (the oldest part of Diriyah), the At-Turaif WHS, and the Diriyah Defensive system. From over 400 samples collected across Diriyah, those from these key sites offer the unique opportunity to study original building techniques and materials that have not been affected by the 20th century reconstructions in the area. Building archaeology and archaeometry methodologies, combined with extensive visual observation, have enabled the identification of recurring building typologies. These typologies have been categorized also based on their building function, location within the settlements, availability of local resources, cultural and social aspects.

3. Preliminary results for the characterization of mortars and adobe in At-Turaif, Ghasibah, Defensive System

Extensive laboratory analyses, primarily conducted in Italian laboratories (University of Florence, University of Padua, CNR), have provided detailed insights into the material composition. Preliminary results include the identification of the source of the earthen materials, localized from the Wadi Hanifah wetlands, characterized by a high silt content and limited clay fraction. This composition significantly influences the material's workability, strength, and durability. Most of the samples show that sand aggregates constitute approximately 50% of the earthen mix. Particle size distribution analysis reveals a significant presence of both fine granules and larger particles, contributing to a reduced average particle size. This bimodal distribution likely influences the material's packing density and porosity. Substantial quantities of coarse aggregates appear to have been intentionally added to enhance mechanical strength, durability, and resistance to the harsh environmental conditions, including thermal stress and erosion. These aggregates play a crucial role in the material's long-term performance. The presence of natural fibers is limited (up to 2%), which is uncommon in traditional earthen architecture. This low fiber content is likely attributed to the structural contribution of the added stone aggregates in mitigating thermal stress and shrinkage-related cracking.

Analysis of decay patterns revealed that the primary deterioration mechanisms are erosion caused by water ponding and subsequent rising damp and wind action. While the inherent properties of the materials and construction techniques offer some resistance, alterations to the original built form or setting exacerbate decays. Areas affected by historical events, such as bombardment during the 1818 siege, debris accumulation at wall bases, and the absence of roofs, exhibit concentrated deterioration.

4. From characterization to conservation

Based on the material characterization, the DF team conservation approach prioritizes the development and testing of compatible replacement materials, minimizing the use of chemical treatments due to their potential incompatibility with the earthen fabric and the harsh environmental conditions. The conserva-

tion strategy focuses on a) the use of sacrificial earthen layers that act as a buffer, protecting the original fabric from further deterioration; b) structural consolidation techniques employing compatible earthen materials and wooden elements to stabilize critically instable elements; c) replacement of decayed materials with compatible but subtly distinguishable ones, such as for instance through the incorporation of polypropylene fibers, ensuring reversibility and facilitating future interventions.
This integrated approach promotes a philosophy of continuous care, minimizing the impact of the conservation interventions on the existing structures, preserving their sustainable characteristics and therefore maximizing long-term conservation outcomes

5. Conclusions

This paper represents the first comprehensive, multi-site study of its kind in the region (Kingdom of Saudi Arabia), that focuses on structures and buildings that have been built within a tightly defined historical period, specifically between the 16th and 18th centuries. The study highlights the unique characteristics of this vernacular architecture, its inherent sustainability, and its adaptation to the harsh climate. Furthermore, it demonstrates how scientific analysis of building materials can directly inform and enhance conservation practices, providing a model for the conservation of similar earthen heritage sites.

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How do we study historic gypsum plasters? A review of current analytical approaches

Although research into historical/traditionally fired gypsum plaster technologies has increased significantly in recent years[1], gypsum remains far less understood than lime and earth plasters[2]. The study of historichistorical gypsum plasters may also be complicated by researchers' greater familiarity with the properties of modern industrial gypsum, even within the field of cultural heritage. This can result in preconceptions when approaching the study of traditional gypsum materials, which may in turn lead to flawed experimental design and interpretation.

This paper will open by briefly defining differences between traditional and industrial gypsum plaster production, composition, and properties. It will then review current analytical strategies for the study of historical gypsum plasters, emphasizing the main questions asked about these materials and the most effective methods for answering them. This will include a discussion of the role and design of replica plasters or reconstructions in analytical strategies, which can allow for the exploration of plaster working properties and inform the interpretation of analytical results from historical plasters.
The most commonly used analytical strategies can be divided between those which assess the working properties of fresh plasters created to replicate historical formulations, and those which evaluate set plasters (historical or replicas). The following methods will be discussed:

Setting processes of fresh replica plasters:
- Evaluation of setting times and mechanisms, including methods such as Vicat needle and calorimetry[3].
- Hydration in real time, using SEM and x-ray tomography[4].

Characterization of set plasters (historical and replicas):
- Chemical analysis of components, including methods for determining composition, firing history, and material origin using XRD, FTIR, Raman, PLM, SEM-EDX[5].
- Microstructural analysis to explore particle morphology, processing methods, original water content[6].
- Accelerated aging tests to simulate long-term evolution of plaster composition and microstructure[7].

In all cases, sample preparation methods and formats will be considered. The adoption of methods recently developed for the study of industrial gypsum plasters will be discussed, as will the adaptation of standardized tests to the study of traditional gypsum plasters. While the focus of the review is the study

1 E.g. Ducasse-Lapeyrusse, Vergès-Belmin 2021 ; Elert, Bel Anzué, Burgos Ruiz 2023; Le Dantec 2019 ; Mishmastnehi et al. 2023; Sagaradze et al. 2023.
2 Ducasse-Lapeyrusse, Vergès-Belmin 2021, 2; Freire et al. 2019, 512.
3 E.g., ASTM 2020; Lewry, Williamson 1994.
4 E.g. Fantou et al. 2024; Seiller et al. 2021.
5 E.g. Schmid, Dariz 2019; Dariz et al. 2022; Jarzyna et al. 2022.
6 E.g. Freire et al. 2019; Lenz 2022. Franceschi, Locardi 2014; Ducasse-Lapeyrusse, Vergès-Belmin 2021.
7 E.g. Elert et al. 2023.

of historic gypsum plasters, many of the issues/considerations it raises will also be relevant for the design and testing of gypsum-based conservation plasters.

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Technological and Architectural Transitions in the Mosque of Old Dongola: A Study of Nubian Wall Painting Techniques

1. Introduction

Study area: information about the archaeological site
Old Dongola, a major urban center of medieval Makuria, is located on the eastern bank of the Nile between the Third and Fourth Cataracts in present-day Sudan. Archaeological research has been conducted there since 1964 by the Polish Centre of Mediterranean Archaeology, University of Warsaw, initiated by Professor Kazimierz Michałowski and now led by Professor Artur Obłuski. The site includes the citadel, the Monastery of St. Anthony (Kom H), and several churches[1]. Key findings include richly decorated monastic interiors featuring Eastern Christian iconography intertwined with portraits of Nubian elites, illustrating a fusion of local and Christian traditions[2]. Conservation of the a secco paintings executed on mud or lime plaster has been conducted parallel to ongoing excavations.

2. Assumption of the project

The mosque in Old Dongola, a reused Christian-era structure transformed into a mosque in the 14th century, preserves stratified wall surfaces that document changes in architectural function and decorative practices. As part of the project "Baraka: Revitalization of the Oldest Preserved Mosque in Sudan – the Mosque of Dongola," funded by the ALIPH Foundation, comprehensive conservation and analytical studies were carried out in 2023 to examine the composition and chronology of plasters and mural painting layers. The project's goal is to trace the architectural and functional transformations of the building—from Christian to Islamic periods—using archaeometric methods, including mortar analysis and dating.

3. Methodology

In 2023, systematic archaeological research of the mosque was conducted alongside architectural, construction, and conservation documentation. The first stage involved stratigraphic tests inside the mosque, revealing construction phases and providing material for further analysis. Forty plaster and pigment samples of plasters, whitewashes, and polychrome fragments were collected and examined usingsubjected to analytical techniques including SEM-EDS, FTIR, GC-MS, variousUV/VIS light microscopy methods, and radiocarbon dating. (AMS). Stratigraphic testsprobes were carried out at 37 points, with special focus onplaced in key locations of the building (Central Hall, staircase, helping to identify chronological construction phases and area). Four samples containing preserved organic material (S14, S16, S22, S47) were selected for radiocarbon dating.

1 Godlewski 2013, 7–8.
2 Martens-Czarnecka 2011.

Figure 1. Mosgue building. Author: M. Skarżyńska

Figure 2. Stratigraphic test ST.M. 13/F28. Authors: A. Chlebowski, A. Kwiatkowska, M.Skarżyńska.

4. Results

Analyzed plasters were lime-mud composites, composed of clay matrices with added lime ($CaCO_3$) and mineral aggregates, including quartz, feldspars, and limestone. SEM-EDS confirmed a heterogeneous microstructure and the presence of Si, Al, Ca, Fe, K, Mg, and Ti in varying proportions. Numerous samples included organic fillers, such as finely chopped straw, cereal chaff, grass stems. Two types of whitewash layers were distinguished: Lime-based, strongly reactive to HCl and composed predominantly of calcium carbonate (e.g., samples S21, S43, S41); Clay-based, composed of kaolinite, non-reactive to acids, detected in samples such as S27 and S50. Confirmed pigments included: Iron-based compounds: hematite (Fe_2O_3) and goethite (FeOOH), used for red and yellow tones; Copper-based green pigment: atacamite ($Cu_2Cl(OH)_3$) identified in sample S38; Green earth (based on Si, Al, Fe, K content), present in selected layers. GC-MS analysis revealed the presence of egg-derived proteins (ovalbumin, lysozyme) in several paint layers (e.g., samples S46 and S51), confirming the use of protein-based binders compatible with a secco technique. In some cases, minor traces of plant-based polysaccharides (possibly gum arabic) were identified. No organic binders were detected in plaster matrices. According to the Radiocarbon Dating analysis our plaster samples provided a chronological framework for construction and decorative phases: S47 and S22, collected from base plaster layers directly on brick in the staircase area, date to the late 7th to 9th century CE, possibly corresponding to early construction phases of the building; S16, from a layer with Arabic inscription, dates to 1166–1220 CE, and must postdate the Christian decorative phase it covers; S14, from a superimposed plaster layer, dates to 1516–1645 CE, likely linked to a Funj-period renovation.

5. Conclusion

The study confirms the consistent use of lime-mud plasters with mineral and organic fillers, and a secco painting technique employing protein-based binders and simple mineral pigments. Despite religious and functional changes, core material practices remained stable. Radiocarbon dating, combined with stratigraphic analysis, provides a reliable framework for reconstructing the building's transformation over time and informs its ongoing conservation.

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Plaster Application Marks and Their Function in the 16th Century Great Siege Wall Painting Cycle, Valletta, Malta

1. Introduction

The Great Siege wall painting cycle in the Grand Master's Palace, Valletta, Malta, was created by the Italian artist Matteo Perez d'Aleccio between 1576 and 1581. Painted in the fresco technique, the cycle has a total area of 225 m2 and depicts the events of the 1565 Great Siege of Malta in twelve narrative scenes. Previous studies of the indicated that the lime plaster was applied in giornate over the highly absorbent Globigerina Limestone support, in a single, thin (~4-5 mm) layer[1]. Only limited analysis of the plaster was carried out.

This paper reports on the examination and analysis of plaster application marks and plaster composition of the Great Siege wall paintings. The research was carried out as a graduate dissertation[2] and contributed to the conservation of the cycle, implemented from 2018-2023 by the Department of Conservation and Built Heritage (DCBH), University of Malta. The study explores plaster application marks, possible adaptation of the plaster composition to the Maltese material context, potential correlation between the plastering technique and its condition, and conservation implications.

2. Methodology

The study was conducted using complementary non-invasive and invasive methods. In the first phase, an examination of the types and distribution of plaster application marks and giornate was carried out using visual examination, photography, and mapping. Plaster application marks were categorized according to their morphological characteristics, time of application, and possible function. Giornate and tool mark distribution maps were then superimposed on condition survey maps to observe possible correlations between plaster application and its condition.

Based on the results of the non-invasive phase of the study, invasive sampling of the original plasters was carried out to understand their physico-chemical characteristics; the distribution of plaster types throughout the painting; and the relationship between plaster application, composition, and current condition. Due to the significance of the painting, sampling was limited to six micro-stratigraphic samples of paint and plaster layers, taken from the areas of already existing cracks or losses, avoiding areas of the past restoration. Samples were prepared in thin section and analyzed using PLM and SEM-EDS to characterize mineralogical composition of the plasters, porosity and binder:aggregate ratios[3].

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1 Leitner 2002; Department of Conservation and Built Heritage 2020.

2 Gorodetska 2022.

3 Thin section preparation and petrographic analysis carried out in 2021 by Pro Arte s.n.c. analytical laboratory, Noventa Vicentina, Italy. The thin sections were further examined in the DBCH laboratory using SEM-EDS.

3. Results and Discussion

3.1 Results of non-invasive investigations

Variations in plaster application were observed throughout the cycle. Some plasters (Type A) had a rough surface texture and tended to be applied in narrow pontate which cut through compositional features. Others (Type B plasters) were smooth and well-compacted, and applied in large giornate which followed the painted composition. Three application marks were frequently observed in plaster surfaces: striations, depressions and plaster reductions. In fresh plaster surfaces, clusters of long, thin (~1 x 60 cm) striation marks were created through repeated smoothing during initial plaster application. Large (~6 cm ⌀), rounded depressions with soft edges resulting from localized pressure on the plaster surface were likely intended to enhance adhesion between the plaster and the underlying stone support. In Type A plasters, abraded surfaces near joins indicated that the plaster thickness was intentionally reduced to provide better adhesion between giornate. Small (~3 cm ⌀) depressions were also made in semi-dried Type A plasters, especially at the edges of giornate, suggesting challenges during application which required specific solutions to mitigate detachment.

3.2 Invasive phase

PLM and SEM-EDX analysis of thin sections of Type A and Type B plasters revealed that differences in surface texture and application methods corresponded with variations in plaster composition: Type A plasters were found to be more porous than Type B plasters (21-25% v. 16-18%) and composed mainly of carbonate aggregates (e.g. shells and crushed limestone) ranging from 40-1500 µm. Type A plasters had low cohesion and micro-cracking was frequent, suggesting shrinkage of the Type A plasters during application and setting. In contrast, Type B plasters contained 28-59% carbonates, a significant proportion of hydraulic terracotta particles (26-58%), contributing to their greater mechanical strength, and small amounts of quartz (1-1.5%). The aggregate sizes in Type B plasters varied from 60-1000 µm, with a notable concentration of 250-500 µm particles. The binder content was also higher than in Type A plasters (40% v. 28-33%), resulting in a denser plaster with improved cohesion.

The uneven particle size distribution and lower binder content in Type A plasters likely led to poor working properties, complicating their application. These issues were not observed in Type B plasters, which contained hydraulic aggregates, an even particle size distribution, and high lime content. The composition of Type B plasters allowed them to be carefully smoothed and compressed during application, resulting in greater adhesion and cohesion than the Type A plasters.

The significant differences in tool marks in the plaster surfaces reflect the variations in composition and quality, resulting in distinct working properties. This suggests that adjustments in plaster application methods, such as dividing the plaster into narrower pontate and utilizing tool marks in semi-dry plaster, were intentionally made to address the challenges encountered with Type A plasters. While the findings highlight a clear interdependence between plaster composition, working properties, and tool marks application, there is insufficient evidence to fully understand the reasons behind the variations in plaster composition throughout the cycle, indicating a need for further research on this topic.

4. Conclusion

The study investigates the role of tool marks in the plastering technique of a large-scale Great Siege wall painting cycle, prioritizing non-invasive investigations. It explores implication of the material properties on plaster application technique and begins to address the issue of possible impact of the plastering technique on the condition of the paintings and associated conservation implications.

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Topic 5

Historic Portland cement-air lime mortars. Historic Portland cement mortars

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Fixing Materials of Czechoslovak "Socialistic" Mosaics

Monumental mosaics from Czechoslovakia's socialist era (1948–1989) have long faced societal rejection due to their perceived association with political propaganda. However, recent shifts in cultural heritage perspectives have led to their recognition as historical monuments, underscoring the need for precise material characterization to develop appropriate conservation strategies. This research addresses the existing gap in knowledge regarding the composition and fixation techniques of these mosaics using standard analytical methods, including scanning electron microscopy (SEM-EDS), thermal analysis (TG/DTG), X-ray powder diffraction (XRD), gas chromatography (GC), and infrared spectroscopy (FTIR).

During the latter half of the 20th century, numerous monumental mosaics were created across socialist countries[1]. In Czechoslovakia, most mosaic installations were produced by two state-run companies due to the absence of private art and craft studios[2]. The largest mosaic studio existed within the so-called Central Art and Craft Studio (Ústředí uměleckých řemesel - ÚUŘ). It developed standardized techniques for mosaic fixation[3]. However, until now, no scientific verification has been conducted to assess the extent to which these standardised procedures were consistently applied in practice.

Fixing materials, i. e. mosaic beds of 10 mosaics designed by outstanding artists of the time (Martin Sladký, Radomír Kolář, Sauro Ballardini, Eva Kmentová etc.) were investigated within this study. Detailed examination of the mosaic samples, including those assembled by state-run studios as well as rare works produced directly by independent artists, reveals both uniformity and notable exceptions in material composition. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses demonstrate that the chemical composition of the mortars generally aligns with expectations for Portland cement binders, with characteristic levels of CaO, SiO_2 and Al_2O_3, and the presence of unhydrated clinker residues. The binder of the ÚUŘ mosaics can be characterised as a blended cement as it contains unreacted blast furnace slag grains apart from clinker residues. This finding is in accordance with contemporary literature[4]. In several samples, a relatively low degree of carbonation was observed, while others exhibited pronounced decalcification and secondary formation of $CaCO_3$ polymorphs such as vaterite and aragonite. In particular, the mortars associated with some state-run projects display a standardised, nearly uniform aggregate composition, whereas authorial exceptions—such as the mosaic sculpture by Eva Kmentová and Olbram Zoubek—reveal the deliberate incorporation of asbestos cement and tailored binder modifications (Figure 1).

Mineralogical analysis using XRD supports the microscopic observations by confirming the presence of unhydrated clinker phases, typical calcium carbonate polymorphs that signify the carbonation of hydraulic binders. Notably, one of the mortars, extracted from the core of Kmentová's mosaic sculpture, exhibits an anomalously high CaO content, which may indicate a binder comprising a mixture of Portland cement and lime. Thermal analysis via TG/DTG further corroborates these findings. Characteristic

1 Koch, Galstyan 2019; Maleschka 2019; Stępień 2021.
2 Říhová, Křenková 2022.
3 Tesař, Klouda 1988.
4 Ibidem.

peaks corresponding to the dehydration of C–S–H phases, gypsum and portlandite were observed in most samples with variations in the degree of thermal decomposition further underlining differences in binder composition and the extent of carbonation. The study also provides insights into the utilisation of synthetic organic admixtures. Gas chromatographic analysis of one façade mosaic sample (Sladký´s stone mosaic "The Architect´s Reason and Sense") revealed the presence of fatty acid esters, which are not in accordance with the expected composition of traditional linseed oil used in the past[5]. Instead, the detected compounds—dominated by saturated fatty acids such as stearic acid, and an anomalously high concentration of erucic acid—suggest the deliberate addition of an artificial mixture, possibly derived from fatty acid salts used as waterproofing agents. Such water emulsions of fatty acid salts had been patented and commercially sold in Czechoslovakia since mid 1960s[6].

Apart from inorganic binders, non-cement fixing materials based on polymer resins were applied. These methods did not appear to represent the preferred standard solution for mosaic fixation. Nevertheless, the use of polymer resins as a mosaic bed was not uncommon, although the durability of works created in this way is significantly lower compared to mosaics fixed in mortar beds. In this study, we characterised mosaic beds based on epoxy resin (with epoxy poured in multiple layers into a metal frame, each layer interleaved with jute) and fibreglass, composed of glass fibres and polyester resin.

In summary, the comprehensive investigation confirms that the mosaic mortars produced during the socialistic period predominantly employed standard blended Portland cement-based mixtures with the supplementary addition of blast furnace slag. These mortars were generally prepared following uniform, centralised procedures as dictated by state-run workshops. Nonetheless, notable deviations from the standard practice, such as the incorporation of asbestos cement and non-traditional organic additives, point to the existence of authorial variations tailored to specific artistic or functional requirements. These findings not only contribute to the broader understanding of late-20th century mosaic production techniques but also provide a valuable reference for future conservation and restoration efforts of socialistic cultural heritage.

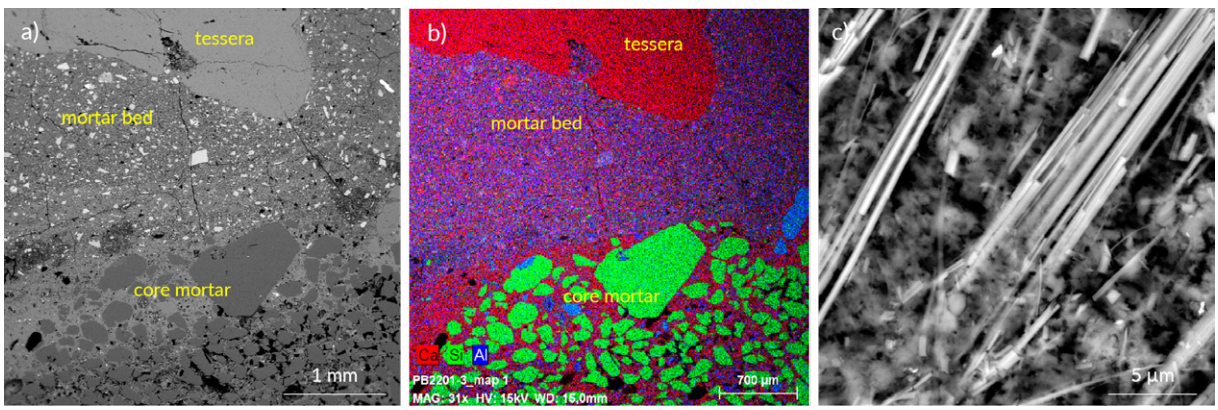

Figure 1. SEM-EDS micrographs of Eva Kmentová´s mosaic statue – (a) a cross-section through the uppermost layers (carbonate tessera, mortar bed consisting of Portland cement and slag and underlying core mortar with silicious aggregates), BSE regime; (b) EDS elemental distribution of Ca (red), Si (green) and Al (blue) within the cross-section; (c) amphibole asbestos identified in the concrete constituting the statue´s body, BSE regime.

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5 Bauerová et al. 2021a.
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An insight on the decorative and finishing renders of the facades of interwar period buildings in Athens, Greece

1. Introduction

The architecture of the first decades of the 20th century, until the 1940's, in Athens, presents a transitional style influenced by the international modernism movements. The transition from Neoclassicism and Eclecticism to Modernism, is expressed, not only in the type of decoration of the facades of these buildings, but also through the selection of the finishing renders used to form these architectural elements. The technological advancements brought by cement in the early 20th century enhanced versatility in composition and form, making these decorations characteristic of the era—particularly a type of render known in Greece as artificiel[1].

These renders participate in the primary composition of the buildings, as the architects of the time, knowledgeable about materials, fully exploit their ability to be freely shaped in various ways, cast in moulds, applied by a trowel with a flat finish, carved or even polished etc. In many cases, in the absence of other decorative expressions, as the modernism movement dictates, the material itself stands as the only decoration. This key feature of interwar structures is often lost or obscured during renovations, as renders are frequently coated with acrylic paints—contrary to their inorganic nature and often in colors that differ from the original.

Figure 1 & 2. Anastasis Metaxas' Hellenic Telecommunications building (1930-1931) in central Athens preserves the original decorations

1 Derives from the French term Pierre Artificielle, which translates to artificial stone

This study focuses on the coloured renders, applied in buildings designed both by noted architects and anonymous ones from the same period, in order to identify and document their composition, their characteristics and use.

2. Methodology

Five significant historical buildings/listed monuments according to the Greek law, from the 1920's and 1930's were studied, focusing on the use of decorative mortars on the facades of the buildings and on individual decorative elements on them. The criteria for selecting the buildings under examination was the preservation of the original materials on their facades. The buildings as well as the samples included in this study, are listed on table 1. Samples were obtained (EN 17543:2021) from representative facade areas and from individual decorative elements.

In order to characterize the samples, the following analytical techniques were applied: Thin-section microscopy for the petrographic analysis, X-Ray Diffraction (XRD) and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) to identify aggregate-binder ratio, microstructural characteristics and determine mineralogical composition, Thermogravimetric Analysis (TGA) to assess binder composition, including lime and cement proportions and finally particle size distribution of the aggregates. Regarding the appearance of the finishes, colorimetry was used to identify the shades in the CIE Lab System and documenting, when possible, the chromatic scheme of the building. Complimentary to the process, historical research was contacted, including archival records and original construction documents, to contextualize the findings.

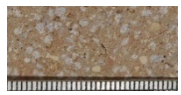
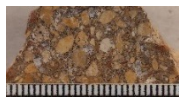
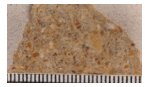
	Building	Date	Architect	Sample	Location	Image
1	El. Venizelos House	1932	An. Metaxas	Ocher coloured render from flat surfaces of the upper structure	SE elevetion	
2	El. Venizelos House	1932	An. Metaxas	Ocher coloured render from the 1st floor cornice moulding	SW elevation	
3	El. Venizelos House	1932	An. Metaxas	Red ocher coloured carved render from the base zone of the building	NW elevation	
4	Hellenic Telecomunications Organization Building	1932	An. Metaxas	Umber coloured carved render from the base zone of the building	N elevation	
5	Themistokleous & Notara Apartment building	1927	N. Nikolaides	Red coloured terrazo-like render from the base zone of the building	N elevation	
6	Massalias & Skoufa Apartment building	1926	N. Nikolaides	Umber coloured render from the entrance of the building	S elevation	
7	Kypselis Apartment building	1920-1930	Unknown	Light ocher coloured polished render from the columns of the entrance hall	S elevation	

Table 1. Building list, samples location and characteristics

3. Results and Discussion

The samples show variations in binder types, with some employing traditional lime-based mixtures, while others incorporate early formulations of Portland cement for enhanced durability. The durability of the mortar reflects its use: renders with larger aggregates (2-3mm) and cement were mostly used on cast and carved elements while smoother, paste-like lime-based renders, with fine aggregates (<2mm) were used to achieve a stucco-like effect covering flat expanses of the facades. In all of the cases crushed calcitic aggregates were used reflecting regional material availability. The similarities in the choice of aggregates combined with the multiple application methods to achieve different textures from carved to well polished according to use, indicates a formation of a technique spread among the craftsmen.

4. Conclusion

The study of 1920's-1930's decorative coloured renders and finishes provides valuable insight into their material properties. Understanding the original materials is crucial for developing conservation approaches that maintain architectural integrity, while ensuring compatibility. The documentation of original renders on the facades of listed buildings sets a scientific basis for restoration guidelines to architects and conservators. Future research should explore experimental replications of these mortars and assess their long-term performance under environmental stressors.

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ArtCim project: characterization and restoration of the decorations in rocaillage and faux-bois cement from the 19th to the 21st centuries. First results of historic study and field survey

1. Introduction

The decorations in rocaillage[1] and faux-bois cement in gardens constitute in France an abundant cultural heritage, but yet unknown, especially in its materiality. Picturesque, popular and bourgeois at the same time, this art of trompe-l'oeil developed strongly in France in the middle of the 19th century, with the appearance of industrial cement and reinforced concrete. Parks and gardens throughout France are equipped, thanks to reinforced cement mortar, with false caves, kiosks, stairs, bridges, railings, benches, imitating nature, stone, but especially wood in all its essences. These constructions are essential elements of landscape walks. Today, this heritage suffers from many degradations, mainly related to corrosion of the reinforcement in mortars and concretes. The lack of analysis and fine characterization on the forms, textures, and materials used makes it difficult to restore and preserve these decorations in a respectful manner. The ArtCim project is interested in this forgotten architecture, first of all by researching the techniques and know-how of the rocaillage craftmen and by adopting a multi-scale approach to characterize it: from site to laboratory, from macro to microstructure. In a second step, different materials and restoration techniques will be tested for maximum preservation of historical materials.

The scientific objectives of the ARTCIM project are:

- To study the know-how, techniques and materials used by rocaillage craftmen, from the 19th century but also used since the 2000s, through a transdisciplinary historical, landscape, architectural approach and analyses, in situ and in laboratory. The know-how of the nineteenth century will be compared with the current culture of rocaillage gardens and the main achievements of the last twenty years.
- To identify the various pathologies affecting this heritage, as well as the influence of the environment on their aging, with non-destructive techniques directly in situ, and laboratory analyses on samples.
- To test different restoration techniques (cleaning, mortars) and evaluate the effectiveness and implementation of new sacrificial anodes to fight against corrosion of frames in rocaillage decors.

2. First results of historic study and field survey

A first phase of historical research[2] identified the inventories of rocaillage decorations already made in France. Detailed research were then carried out on the implementation techniques and materials used (cement, binder, reinforcement, wire mesh, aggregates, additives...), as well as on the catalogues of rocaillage craftmen. This research were carried out through consultations of various archival resources but also through meetings and interviews with the associations for the valorization of this heritage, as well as the rocaillage craftmen in activity.

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1 Rocaillage is the French term for the use of cement to create artificial rockwork or wood, trying to imitate the natural disposals, in a new development of the long tradition of Rusticage, a attempt to use grotto and wild world aesthetics.
2 Gourguechon 2024.

From the 1980s in France, Michel Racine will publish preliminary works on general inventories and rocaillage craftsmen, with surveys carried out in the region of Marseille, in the Lot, the Creuse, but also from a national point of view[3]. In Marseille in particular, the inventory of rocaillage heritage is completed by interviews with the Gagliardone family, which counted four rock makers from the 19th to the 20th century, and how the know-how was passed on. In horticultural journals, many reports are published on the construction of rocks, caves with stalactites, railings. Opinions are given on the aesthetic quality of the installations but also on the materials and techniques used, and details on costs. The use of Vassy cement and Portland cement is thus found. In the patents, colouring techniques are proposed by mixing cement with very finely ground iron oxides or mineral salts with oils to paint cements and imitate wood. The major construction sites of the Parisian parks, from 1854 for the redevelopment of the Bois de Boulogne, then from 1863 for the park of the Buttes-Chaumont, or the universal exhibitions, were pioneers in the use of cement in the manufacture of fake rocks and faux-bois. Historical documents, such as calls for proposals or quotations, sometimes include interesting plans and sketches.
Thanks to the inventories found, 30 sites were visited, spread across France and over a long period of implementation, allowing us to obtain a representative panel of the major areas of rocaillage (Île-de-France, the Côte d'Azur, Isère, Bordeaux and its nearby region, and Normandy). The regional differences but also on construction periods were thus characterized. Feedback on the restoration of these decorations was also studied. On the sites visited and studied, many types of cement decorations were found: caves, waterfalls, false rocks, decorated path, basin, pier, kiosk, hut, bird house, bridge (Figure 1), railing, stairs, flower pot, fountain, grave, benche, and false ruins. Many remains of polychromy have been observed, especially in the south of France, where the climate is drier and therefore less conducive to biological coatings. The conditions of these sets are very variable, from very good to very altered, sometimes even the total loss of the elements. Corrosion of the reinforcement is the main source of damage, ranging from a crack and chipping to the spalling and loss of the original material (Figure 2). Biological coatings also contribute to alterations, especially in the reliefs and surface roughness, with a gradual loss of texture of the decors. In the underside of roofs or caves, chemical dissolution facies are also present, related to problems of waterproofing or preferred water flow (Figure 2). The proximity of plants and trees can also cause more mechanical alterations, with cracking and breakage, due to growing roots or stems, or falling trees. The majority of restorations performed are of low quality, with color and texture incompatibilities, and cracks at the original repair/material interfaces. A few examples of restoration are very interesting, with work on aesthetic integration.
Of these 30 sites visited, 6 were chosen for a complete characterization and diagnosis, in situ and in the laboratory on samples. Prospective restoration tests will also be implemented in a second part of the

Figure 1: Bridge in faux-bois in Moulin d'Andé garden (Normandy – France). © LRMH

Figure 2: decay of a kiosk roof underside in the park of the Buttes-Chaumont (Île-de-France – France). © LRMH

3 Racine 2001.

ArtCim project, in order to find preliminary solutions and help protect this exceptional cultural heritage.

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ArtCim project: characterization and restoration of the decorations in rocaillage and faux-bois cement from the 19th to the 21st centuries. Case study of the Faremoutiers abbey park in France

1. Introduction: The ArtCim project

In France, the decorations in rocaillage[1] and faux-bois cement form a rich yet largely overlooked heritage, particularly in terms of their material composition. Positioned at the intersection of the picturesque, the popular and the bourgeois, this illusionist art flourished in the mid-19th century, driven by the industrialization of cement and the rise of reinforced concrete. Parks and gardens were embellished with artificial caves, kiosks, staircases, bridges, railings and benches imitating stone, natural elements, and most notably, wood in all its forms. These constructions played a key role in shaping the aesthetics of landscaped promenades. Today, however, this heritage faces widespread degradation, primarily due to the steel reinforcement corrosion in concrete and mortar. The ArtCim project seeks to advance knowledge of this long-neglected heritage through a multidisciplinary approach. It combines historical, landscape and architectural studies with multi-scale analyses of these elements, ranging from imaging technologies (3D scanning, photogrammetry) to physico-chemical material characterization in-situ and in the laboratory on samples.

Following an extensive field survey, six sites were selected for the study, spread across France and covering a wide implementation period, providing a representative sample of the main regions of rocaillage (Île-de-France, Provence-Alpes-Côte d'Azur, Bordeaux and surrounding areas, Normandy). Among these sites is the park of the Faremoutiers Abbey, which is the subject of the case study presented here.

2. Historical context

The Notre-Dame de Faremoutiers abbey is located about 60 km east of Paris in France. It was founded around 620 by Saint Fare but was largely destroyed, mainly during the French Revolution. In 1885, the owners, Mr and Mrs Méric de Longueil, transformed the 15-hectare garden into an English-style landscaped park. In 1903, Georges Combaz (Combaz Frères) was in charge of the realization of two reinforced cement structures in faux-bois style: a kiosk (Figure 1) and an embankment on the pond. He came from the family of the famous rockworker Eugène Combaz (1824-1881), renowned for his work on the artificial rocks in the Parc des Buttes-Chaumont in 1867. The embankment on the pond can be compared to the garden sheds built at the same time in the Parc des Buttes-Chaumont by the same company[2]. The faux-bois decorations on the garden features a wide variety of wood types and details, demonstrating exceptional craftmanship: railings and pillars made from faux-bois logs, facings in faux-bois planks, imitating bamboo and even millstone. Many traces of polychromy can be seen on the decorations.

1 Rocaillage is the French term for the use of cement to create artificial rockwork or wood, trying to imitate the natural disposals, in a new development of the long tradition of rusticage, an attempt to use grotto and wild world aesthetics.
2 Gourguechon 2024.

3. Characterization of the faux-bois cement decorations

3.1 Analysis protocol

A variety of non-destructive analysis methods, more commonly applied on concrete flat surfaces, were tested on the different topologies of decorations found on the site, which presented highly irregular surface conditions. The tests aimed to assess the suitability of these methods and develop an analysis protocol tailored to the in-situ study of the rocaillage heritage. The investigations focused first on the macroscopic structure itself (including its links with the environment, dimensions, and shapes), followed by an examination of the epidermis (texture, color), and finally, the stratigraphy of the materials at depth. Photogrammetric surveys and 3D digitization were carried out to capture the texture of the decorations in as much detail as possible. Remnants of polychromy on the decorations were identified, and a colour survey was performed using a colorimeter. The stratigraphy of the materials was analysed in the field using non-destructive methods, including a pachometer and a ground-penetrating radar. Further tests were carried out to assess the transfer properties, including water absorption (via the sponge method) and their mechanical properties (compressive strength using a sclerometer). Electrochemical measurements were also carried out to characterize reinforcement corrosion in the mortars, by mapping electrochemical potentials and measuring resistance to linear polarization (corrosion rate). Finally, a detailed diagnostic was compiled to identify the various forms of deterioration.

Samples were taken from the decorations for further laboratory analyses to characterize the materials in terms of chemical composition, formulations, and physical properties. Observations were carried out using 3D microscopy and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), along with X-ray diffraction (XRD) analysis on powdered samples. These analyses aimed to identify the binders, aggregates, and potential pigments used, as well as any pathological compounds present in the materials. Water and cement contents were measured to determine the precise formulations of the historical mortars. To assess the behaviour of these materials in relation to water, porosity and capillary water absorption tests were conducted. Additionally, the dynamic Young's modulus of the materials was determined through ultrasonic velocity measurements.

3.2 Results overview

The kiosk diagnosis revealed various forms of deterioration, including cracks, swelling, flaking, and spalling, often near reinforcements. The underside of the roof (Figure 2) showed the most severe damage, with significant efflorescence due to water infiltration. Micro-organisms (algae, moss, and lichens) covered the entire structure, and weather-exposed surfaces appeared eroded. Traces of polychromy were mainly preserved on the sheltered interior façades.

The in-situ analyses highlighted the challenges encountered when applying some non-destructive methods—commonly used on flat concrete surfaces—to the elements in rocaillage. The Wenner method for

Figure 1. Kiosk in cement faux-bois in the Faremoutiers abbey park © LRMH

Figure 2. Deterioration of the underside of the kiosk roof in the Faremoutiers abbey park © LRMH

measuring the electrical resistivity of concrete, which relies on four aligned probes, is not applicable to irregular elements such as railings or faux-bois logs. Similarly, the relevance of using the sponge test or the sclerometer can be questioned, even in the flattest areas, due to the numerous surface details imitating insect exit holes or wood grain grooves.
In parallel, the advantages and limitations of both 3D digitization methods (3D scanning and photogrammetry) were assessed. Parameters such as acquisition time, processing time, data volume, point cloud resolution, texture quality, practicality in the filed, ease-of-use and accessibility were compared to establish a precise methodology for the study of this rocaillage heritage. Finally, the characterization of the materials enabled the identification of the different layers composing the cement elements, paving the way for the implementation of effective, tailored restoration protocols.

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Insights from Historical ACR-Affected Concrete: Resistance to Frost Cycles and Chloride Exposure

1. Introduction

Studies on the durability of concrete subjected to a combination of alkali-aggregate reaction (ACR) and freeze-thaw (FT) cycles in the presence of chlorides are typically conducted on test specimens exposed to accelerated ACR product formation in an alkaline aqueous solution at elevated temperatures[1]. However, a key question remains: Are the reaction products formed during accelerated aging identical to those produced under natural environmental conditions? To explore this, the historical concretes of the Rupnik Line bunkers—approximately 85 years old and prepared using limestone or dolostone aggregate—were exposed to FT cycles and chlorides. In the concrete containing dolostone aggregate (DC), the ACR reaction progressed significantly under natural environmental conditions[2,3]. Concrete with limestone aggregate (LC) was used as a reference mixture. Additionally, the research findings were compared to those obtained from laboratory-prepared specimens[1].

2. Materials and Methods

Samples of historical concrete were drilled from the bunkers. Three samples from each composition (DC and LC) were used for testing. FT test in the presence of chloride ions from a 3 % NaCl solution prepared with tap water were conducted in accordance with the standard CEN/TS- 12390[4]– 9 (cube test, alternative method). The samples, immersed in the solution, were kept at a temperature of 20 °C for 8 hours and then frozen at -15 °C for 16 hours. The NaCl solution was replaced weekly. Compressive strength, mass loss and static and dynamic E-modulus were measured every 5 cycles. Additionally, XRD analysis and SEM-EDS analysis were performed after 25 FT cycles.

3. Results and Discussion

3.1 Mass loss

The mass loss during the first 15 cycles was similar for both the DC and LC samples. However, after 20 cycles, the mass loss of the LC samples exceeded that of the DC samples. The maximum mass loss reached 20 mg/mm² for the DC samples and 25 mg/mm² for the LC samples. This significant mass loss in both concretes can be attributed to their poor quality, likely resulting from inadequate workability and/or compaction. This conclusion is further supported by the relatively high deformations observed during static E-modulus testing. Similarly, higher mass loss was noted in laboratory-prepared limestone CEM III/B samples, while the dolostone samples exhibited the highest durability among all tested compositions[1].

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1 Turk et al. 2025.
2 Štukovnik et al. 2020.
3 Turk et al. 2022.
4 Institute for standardisation 2016.

3.2 Change in compressive strength

The compressive strength of the historic samples before FT cycles was 45 ± 5 MPa for the DC samples and 50 ± 6 MPa for the LC samples. This strength was largely maintained during the FT cycles, up to 25 cycles for the DC samples and up to 15 cycles for the LC samples. However, the LC samples disintegrated after 15–20 FT cycles, confirming their lower durability. In contrast, the compressive strength of the laboratory-prepared samples before FT cycles was significantly higher—approximately 80 ± 5 MPa for the LC samples and between 90 and 100 MPa for the DC samples. A drop in strength with increasing FT cycles was consistently observed in the LC samples, whereas the DC samples maintained their compressive strength even under laboratory conditions.

3.3 XRD analysis

XRD analysis of historical LC and DC samples confirmed the presence of conventional cement phases as well as phases specific to the presence of chloride ions, such as Friedel's salt (Table 1). Both samples contained cristobalite and tridymite, which are associated with slag. Additionally, both compositions exhibited high gypsum content, particularly the LC sample from a bunker located at a higher altitude. According to Huang et al.[5], gypsum improves the rheological properties of fresh concrete and may have been intentionally used 85 years ago to achieve lower w/c ratios. Compared to the laboratory-prepared samples, the LC sample showed a higher concentration of the monocarboaluminate phase. In contrast, ACR-affected DC samples displayed a higher concentration of the hydrotalcite phase. The concentration of Friedel's salt was comparable for the LC and DC samples. Overall, XRD analysis confirmed similar reaction mechanisms in the historical concrete and the laboratory-prepared samples.

Sample	Calc. (%)	Dol. (%)	Fried. (%)	Ett. (%)	MC (%)	HT (%)	Port. (%)	Br. (%)	SiO_2 (%)	Crys. (%)	Tryd. (%)	Gyp. (%)
LC	43.7	28.3	2.0	0.6	2.7	0.1	4.7	0.0	0.9	1.8	0.7	14.5
DC	14.5	62.2	2.2	0.2	0.9	4.3	2.0	0.3	1.7	1.0	2.8	7.9

Calc. – Calcite; Dol. – Dolomite; Fried. - Friedel's salt; Ett. – Ettringite; MC – Monocarbonate; HT – Hydrotalcite; Port. – Portlandite; Br. – Brucite; Crys. – Crystobalite; Tryd. – Trydimite; Gyp. - Gypsum

Table 1. XRD analysis of concrete from Rupnik military line

3.4 SEM-EDS analysis

The historical LC samples still contained unreacted cement particles even after approximately 85 years. SEM-EDS analysis also confirmed the presence of secondary chloride and sulfate products. Point analysis revealed the formation of Küzel's salt and thaumasite. In contrast, the historical DC samples exhibited advanced ACR, with the presence of clinochlore and secondary calcite clearly visible. Friedel's salt was detected in the DC samples through point analysis, consistent with observations in the laboratory-prepared samples. The LC samples, on the other hand, showed the formation of Küzel's salt, likely due to the higher sulfate content originating from gypsum. Overall, similar phases were identified in the historical concrete and the laboratory-prepared samples, even when an accelerated aging regime was applied in the laboratory.

4. Conclusions

Studies of freezing and thawing in a chloride solution, conducted on historical concretes from the Rupnik Line, have shown that the deterioration mechanisms in concretes with limestone and dolostone aggregates are comparable to those observed in laboratory-prepared samples subjected to accelerated aging. This similarity is particularly evident in concretes with dolostone aggregate, where highly advanced alkali-carbonate reaction was observed. The findings suggest that the accelerated aging of the laboratory-prepared samples effectively simulated the actual changes caused by ACR in dolostone aggregate

5 Huang et al. 2024.

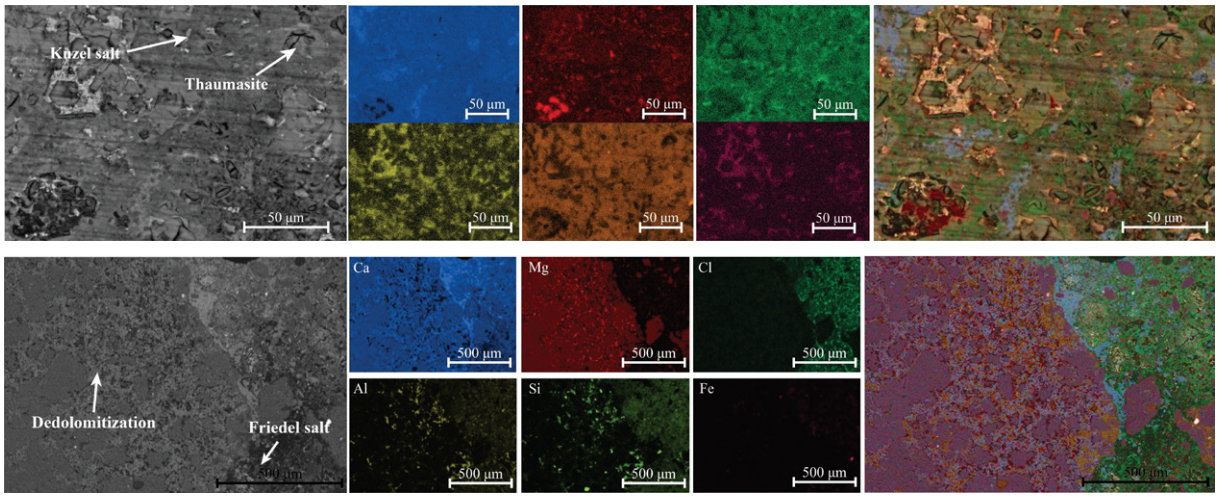

Figure 1. SEM-EDS image of limestone historical concrete (above) and dolostone historical concrete (below)

concretes. It is estimated that the agreement between the results would have been even closer if the same carbonate aggregates used in the construction of the Rupnik Line bunkers had been utilized in the laboratory samples. Furthermore, the presence of cristobalite and tridymite indicates the use of slag in the cement of the historical concretes. Therefore, it is reasonable to compare the results obtained from the historical concretes with those of laboratory-prepared samples made using slag cement.

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Study of the mortars employed by Antoni Gaudí at Casa Batlló

Introduction

The architect Antoni Gaudí and his body of work have been subjects of extensive academic interest. However, the constructive aspects have been relatively underexplored, focusing on only a few specific elements. The renovation, designed and executed by Antoni Gaudí, of Casa Batlló (1904-1906) is one of his most highly classified works: UNESCO World Heritage Site (designated on July 15th of 2005). This recognition requires the highest standards of quality in the conservation and management of the building. Any intervention, no matter how minor, requires an in-depth understanding of the materials, elements, and systems to ensure their proper comprehension and to facilitate the application of the general restoration principles outlined in the Master Plan.

Over the last decade, several maintenance, conservation, and reinstatement interventions have been carried out to restore original elements altered during the mid-20th century. These actions have provided a deeper understanding of the building and have enabled the characterisation of construction systems, ensuring the highest standards of rigour for interventions.

Prior to the interventions, an extensive body of literature on Gaudi's work, including scientific articles, outreach publications, studies and doctoral theses containing relevant information, provided a solid foundation of knowledge. This review framework allowed delving deeper into the strategies employed by Antoni Gaudí at Casa Batlló.

The period during which Antoni Gaudí carried out the renovation of Casa Batlló concurred with a time of transition and transformation of construction materials. The production of mortars and concretes was becoming a fully-fledged industry, and the use of lime as a binder was being increasingly supplanted by others with higher hydraulic properties and enhanced performances. From previous studies, it can be stated that mortars made with lime, natural cement, and Portland cement, across their different variants, coexisted on the market at that time. Gaudí sought to exploit the advantages, qualities, and specific properties he recognised in each of these mortars by applying them across multiple building elements, both in the interior and the exterior.

Casa Batlló serves as an example that reflects the historical evolution of binders used for mortar production in Catalonia during the transition period between the 19th and 20th centuries. Although it cannot be confirmed with certainty whether the inauguration of the first Portland cement factory in Catalonia (Asland in Castellar de n'Hug, 1904), established through the patronage of Eusebi Güell i Bacigalupi, provided Gaudí's access to this new binder, it is well known that Gaudí was neither conventional nor one to miss opportunities to explore the innovations offered by emerging materials and techniques. It is therefore very likely that Gaudí also experimented with Portland cement at Casa Batlló. Indeed, this study found evidence that binders exhibiting a comparable hydraulicity were used during the renovation, which supports this hypothesis.

This research aims to identify multiple mortars used during Antoni Gaudí's renovation of Casa Batlló and, once identified, to characterise the performance requirements as well as establish the techniques employed in their application.

Metodology

The methodology is consistently applied in each analysis of the materials, elements, and construction systems analysed. Based on the hypotheses outlined in the Master Plan, a campaign of sample collection and core extraction is planned. Although numerous cores are extracted, these localised extractions represent only a very small area of the total surface of the renderings. Sampling locations are chosen to minimise damage to the renders, and the number of samples ensures that the data is reliable and the results are representative of the whole.

In the mortar characterisation, samples have been analysed to determine their composition, stratigraphy, thicknesses, colours, and location within the building. The sample analyses were conducted at various laboratories: Materials Laboratory from the Barcelona School of Building Construction (EPSEB), Gabinet del Color and Mineralogy Laboratory from the University of Barcelona. The following tests were carried out to characterise the different mortars: chromatic and stratigraphic analysis using a stereo microscope; particle size distribution analysis; binder/aggregate ratios determination; X-Ray Diffraction (XDR); Thermogravimetry Differential Thermal Analysis (TG/DTA); Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS); and Gas Chromatography–Mass Spectrometry (GC-MS).

To define the construction system, it was necessary to carry out core extractions to expose hidden layers, which complemented the results found. In particular cases, these extractions were fundamental to determine the supporting elements of the finishes or to identify the overall construction system.

Results

The most relevant results of the research are presented below, structured according to the areas of location and function in the building. Among the most significant results, analytical investigations of the main façade revealed a two-layer mortar structure, used as a general treatment for the stone joints and the junctions of the window frames.

This two-layer system consists of a first layer of natural cement mortar and a second fixing layer for the façade coating. The second layer shows a whitish tone, which is composed of lime mortar, and a greyish tone, corresponding to the Portland cement mortar. This mortar system forms an irregular diagonal banded pattern of alternating colours, which had not been previously identified.

On the rear façade, a thin levelling layer made from natural cement mortar was also observed. This material appears to have been employed as a base layer to regulate the undulating surfaces on both the main and rear façades, as well as across many of the interior undulations. Further, on both façades, the fixing mortars for the glass mosaic fragments that compose the trencadís consist of lime, natural, and Portland cement mortars. This same alternation has been confirmed on the rooftop chimneys, both in the mortars used for fixing the trencadís and in those applied renders over the vertical facings.

Inside the residential spaces, the lower sections of the walls are decorated with wooden panelling, while the upper sections of the walls and ceilings feature a lime stucco finish. On the main floor, the lime stucco finish goes beyond the flowing shapes and incorporates a novel and previously undocumented technique, creating a trencadís directly within the stucco. The result is a multitonal lime stucco surface with incisions that delineate the trencadís pattern. These incisions were later filled with lime mortar of a different colour to visually distinguish the joints from the trencadís. These renders are found on both walls and ceilings, standing out for the originality of their design, the tonal variation, and the quality of their execution. On the same floor, the trencadís joints from Mr Batlló's office feature a finish executed with gold leaf.

One noteworthy aspect is the continuous visual effect created by walls and ceilings, where the curved and undulating forms erase the typical sharp edges of masonry construction. The ceiling system itself is innovative, comprising a base layer made of natural cement mortar reinforced with steel metal mesh, without any corrosion protection system, which serves as a substrate for the aforementioned decorative finish. Other small, formable architectural features, such as certain ventilation elements, were resolved using the same material approach.

Lime stucco can also be observed in the common areas, particularly in the original circulation core formed by the staircase and lift that connect the ground floor vestibule and the fourth floor.

Conclusions

This study of the mortars used by Gaudí at Casa Batlló, along with the fresh perspective it provides, deepens on the understanding of the use and development of binders and mortars in Catalonia.

Moreover, the results contribute to advancing the knowledge of the materials applied in construction solutions through current scientific capabilities. This allows for assessing whether the building's architecture is driven solely by formal and design considerations, or whether, on the contrary, it is determined by the structural or performance-related function of each element.

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Topic 6

Heritage-inspired building materials for sustainable architecture: from archaeometry to application

NIGEL COPSEY

Traditional lime rich surface finish mortars, their like-for-like reproduction and their potential contribution to Global Heating Mitigation

Traditional lime mortars for above ground construction were typically made with pure or nearly pure lime and were typically lime rich – and for much of building history, very lime rich. Whilst 2 lime: 3 aggregate and 1:2, as well as earth-lime mortars, were common for building, and whilst even typical building mortars might be lime richer even than this, mortars for surface treatments, such as plasters, pointing and render mortars were richer in lime – 2 lime to 1 being very common before the 19thC[1]. Many plasters and renders were of lime and hair (or other fibre) or even of lime only. Bricklaying mortars in London might be as rich as 4:1[2]. Most of these mortars were initially dry slaked, dry slaked lime exhibiting significantly less initial shrinkage as well as earlier stiffening behaviour than wet slaked or lime putty lime mortars, making their practicable deployment as very lime rich mortars more straightforward. Pure or nearly pure lime mortars as surface treatments will carbonate around 80% in the first two years[3]and develop more compressive strength over time than is generally understood[4]. They will dry building fabric and keep this fabric dry and thermally efficient. Hybrid cement-lime or NHL mortars will carbonate 20% in their lifetimes and Portland cement mortars barely at all. As the production carbon emissions of readily available pure lime mortars – in the form of quicklime, pre-slaked dry and wet hydrates – become negative in the next few years, the like for like repair or reinstatement of lost lime rich traditional surfaces coatings will provide active carbon sinks for the removal of existing carbon dioxide from the atmosphere. As building mortars, and along with traditional earth-lime mortars, they would be perfectly capable of displacing currently used cement mortars for most domestic house construction, greatly contributing to the reduction of construction industry carbon emissions, currently estimated by the United Nations to be 37% globally[5].

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Towards sustainable restoration: a comparative study between shell-based and commercial lime putties

1. Introduction and aims

This research aims to investigate the feasibility of producing restoration mortars, using lime putties manufactured from bivalve mollusc shells, commonly found as a waste from the consumption of the molluscs. Due to their calcium carbonate composition, marine bivalve shells are a potentially idoneous raw material for the manufacturing of calcitic lime. Indeed, these shells are mainly composed of calcium carbonate, under the form of calcite and/or aragonite, formed through a process of bio-mineralization.
To assess the validity of these materials for the production of lime mortars, they have been compared with three commercial limes that are commonly used for the manufacturing of restoration mortars in southern Spain. All quicklimes have been slaked under water in the laboratory following the artisanal process, to obtain comparable lime putties. As these limes are intended to be used for conservation and restoration interventions, their compositional and physical features have been studied in line with the criteria of compatibility, reversibility and durability established for restoration mortars[1].

2. Materials and methods

2.1 Manufacturing and study of the lime putties

Three types of recycled bivalve mollusc shells were selected to produce limes:

1. Ostrea edulis (sample 1), composed mainly of calcite and partially of aragonite.
2. Mytilus galloprovincialis (sample 2), composed of calcite and aragonite.
3. Acanthocardia tuberculata (sample 3), totally composed of aragonite.

To produce the quicklimes, a total of 1500 g of ground shells were calcined in porcelain crucibles at 900 °C for 3 hours (with a temperature gradient of 7°C/min), to ensure complete thermal decomposition of calcium carbonate (CaCO3) into calcium oxide (CaO).
Moreover, three commercial quicklimes of calcitic composition were purchased from the following companies (all from Morón de la Frontera, Sevilla, Spain):

4. Clqlump-CS (sample 4): from the company Cales del Sur.
5. Clqpowder-AN (sample 5): from the company Ancasa.
6. Clqlump-GO (sample 6): from the company Gordillo.

Slaking of the six quicklimes was undertaken under water to obtain lime putties, with approximately 1 L of water for each sample. During slaking the temperature rise was monitored to follow the hydration reaction. The morphological features of limes were monitored under High-Resolution Scanning Electron Microscopy (HRSEM) after 1 and 7 months of aging. After 7 months under water, the rheological behav-

1 Groot et al. 2022.

iour of lime putties was also measured by means of a R/S Plus Brookfield Rheometer (under CSR and CSS mode).

2.2 Manufacturing and study of lime mortars

Mortars were prepared after one year of aging under water of the lime putties. A total of 36 mortar specimens of 4x4x16 cm, 6 for each lime type, were prepared according to the EN 196-1[2], with a pre-mix of the lime putty at slow velocity during 30 s and mixing times of all the components at slow velocity during the first 30 s and fast during further 30 s. A CEN standard siliceous sand3 in a lime:sand ratio of 1:2 by volume was used. The amount of water was determined for each lime and the workability of the mortar was assessed by means of the standardised flow table test[3] . Mortars were demoulded after 10 days and were cured at T= 20 ± 2 °C and RH = 70± 5% for 4 months before their study. The carbonation process of the mortars was followed by means of XRD analyses after 2 and 4 months of curing. After 2 months, the mechanical compressive and flexural strengths were tested according to EN 1015-11[4]. After 4 months, mortars samples were oven-dried for 12 hours at 70 °C and the following hydric tests were performed: free water absorption by total immersion[5], drying[6] and capillary uptake[7] .

3. Results and discussion

All lime putties present many agglomerates of micrometric and sub-micrometric particles, with the hexagonal morphology typical of portlandite crystals. The micrometric portlandite crystals are thicker (~5 µm) and larger (~10 µm) in lime 1 (made from seashells), compared to the rest of limes. All limes follow the Hershel-Bulkley rheological model, but the plastic viscosity and yield stress are very different among them, being these values generally higher in the commercial limes, except for the shell-based lime 3, which showed a rheological curve typical of rheopectic suspensions.

The mechanical and hydric parameters shown in Table 1 indicate that a similar physical behaviour may be expected in shell-based and commercial lime mortars. Based on the low values of compressive strength (Rc ≤ 2 MPa) achieved after 2 months, their use is more recommended for plastering/rendering than for structural applications.

Sample	ρ (g/cm^3)	R_c (MPa)	C_c (g/m^{2}s$^{1/2}$)	A_b (%)	D_i
Mortar 1	1.72±0.02	2.01±0.3	206.64±0.71	11.90±0.23	0.68±0.01
Mortar 2	1.79±0.01	0.99±0.9	307.14±5.36	10.79±0.11	0.69±0.02
Mortar 3	1.68±0.03	0.86±0.05	284.87±2.11	12.58±0.48	0.67±0.06
Mortar 4	1.73±0.01	1.06±0.14	179.75±2.18	10.50±0.16	0.65±0.01
Mortar 5	1.67±0.02	0.73±0.07	264.32±3.96	11.88±0.27	0.70±0.02
Mortar 6	1.70±0.01	0.62±0.09	215.91±1.19	10.97±0.12	0.71±0.02

Table 1. Main physical properties of the mortars manufactured from shell-based (1 to 3) and commercial (4 to 6) lime putties. ρ: bulk density of the mortars after 2 months of curing (in g/cm3); Rc: compressive strength of the mortar samples after 2 months of curing (in MPa); Cc: capillary uptake coefficient of mortars after 4 months of curing (in g/m2s1/2); Ab: free water absorption of mortars after 4 months of curing (in %); Di: drying index of mortars after 4 months of curing.

2 UNE-EN 196-1 2016.
3 EN 1015-3 2020.
4 EN 1015-11 2019.
5 UNI EN 13755:2008.
6 NORMAL 29/88:1988.
7 UNI EN 1925:2000.

4. Conclusions

This study demonstrates that limes manufactured from recycled seashells are totally viable for restoration, providing a sustainable and functional solution depending on the specific requirements of the restoration project. Therefore, further research and in situ testing is needed to verify their long-term performance at different environmental conditions and although these mortars promise to be a sustainable and efficient option, they need to be thoroughly evaluated to ensure their viability in practical restorations.
The production of lime from shells would have a positive environmental impact, as it would reduce the extraction of limestone and, at the same time, it would promote energy savings and waste revaluation, optimising resources according to circular economy. This innovative and environmentally friendly approach aims to convert a waste into an ecological product with high added value, as lime has the capacity to absorb CO2, further minimising the carbon dioxide footprint, not to mention the well-known qualities of lime as a binder in restoration mortars.

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From laboratory to site: Renders of Paimogo Fort, a case study

1. Introduction

The Paimogo Fort, is one of the several Portuguese military fortifications, built in the 17th century, with the intention to protect the Portuguese coastline territory from the constant military threat from the ocean. Abandoned since 19th century, it suffered severe damage. The latest renovation work, carried out in 2006, most of the original renders have been removed and replaced by new ones, based on hydraulic lime mortars, which show significant signs of deterioration, only few years later. Within the scope of the "Coast Memory Fort" EEA Grants project[1], promoted by Lourinhã Municipality, which aims to safeguard and revitalize the Paimogo fort (EEA Grant), new repair mortars for wall renders were developed by the team of National Laboratory for Civil Engineering, that should fulfil the required functions: protection and aesthetics of the Fort walls.

In this investigation, several in situ applications were made on the Fort external area, and their performance was assessed by a multidisciplinary team from different fields, with the aim to select the most balanced render formulations to be applied on the Paimogo Fort walls. The tests carried out to verify their efficacy and their compatibility with the original masonry and environmental conditions are presented; the main axes that structure the action and reflection of the working group for the intervention solutions are described; the final application aspects are presented.

2. Materials and method

The architectural rehabilitation project was inspired by two elements: the formal simplicity of the building, which derives from its military function, and the majestic isolation of the place where it stands, the cliff overlooking the Atlantic and the coastline. The architectural design thus conceived the restoration of Paimogo Fort and the revitalization of the surrounding area as a single gesture, aiming to preserve this heritage for future generations. Based on these considerations, with the aim of giving a new use to the fort without interfering with its original structure, a satellite building was conceived to host an exhibition space, a café, and all the facilities. The architectural design of the Fort was defined with the following principles in mind: Compatibility and Minimal Intervention, aiming to minimize the impact of the new design on the historical building. Distinctiveness, aiming to distinguish the changes introduced, emphasizing the harmony and dialogue between the past and the present. In addition to that, the principles of Reversibility and Repairability strongly guided the design of the building's interior, characterized by removable wood panels and an elevated wood floor, both concealing cables and infrastructures. This approach allowed the walls and vaults to remain intact. Regarding the architectural design, the methodology is based on an interdisciplinary approach that bridges the fields of history and archaeology, aiming to deepen the understanding of the fort's features, functions, and original use. As a result of this method, combined with the creative process, the formal and aesthetic choices seek to establish a clear material and formal continuity with the fort's military function. This is clearly reflected in the decision to combine the rose-

1 EEA Grant.

hued mortars with stone elements that bring an essential contemporary design to the walls, such as the gargoyle and the watchtowers. To materialize these methodology, 6 mortars compositions were applied in real-scale experimental panels in the Fort external area, based on a previous experimental laboratory study[2-3]: The selected mortars were composed by: slaked air lime (A); mix of slaked air lime and quicklime (A+Q30%), being the optimum amount of quicklime previously defined by laboratory testing; a slaked air lime and white cement mortar (C:A) was also considered, due to its application in a similar environment[4]. To approach the original mortar compositions, a natural siliceous sand (0/4mm) from the Tagus River mixed with fine limestone sand (0/1mm) in 10% (L10) and 5% (L5), by volume, was used as aggregate in the render coats. A and A+Q30% mortars were formulated with a binder/aggregate ratio of 1:2, in volume, to approach the high lime content of the original mortars, while in C:A a proportion of 1:3 was used due to the expected higher strength of the binder. All the mortars were prepared in situ and were applied in several coats (fluid spatterdash, 2 render coats and a finishing coat). For each panel, half of the finishing coat was pigmented using an inorganic natural pigment, rich in Fe2O, at a concentration of 2% of the lime weight, diluted in the mixing water, and the other half was left without pigment, for the evaluation of its influence (Figure 1a).
Besides visual observation, an experimental program was carried out with the aim of verifying the compatibility and efficacy of the new mortars, during approximately one year. The following techniques were used: Shore hardness, with Shore A durometer (ISO 7619 and ASTM D2240), Ultrasonic pulse velocity (EN 12504-4), water permeability at low pressure by Karsten tubes (EN 16302) and adhesion between layers and to the substrate by pull-off (EN 1015-12).

3. Main Results and Discussion

The main results show that mortars with slaked air lime (A:L10 and A:L5) present the lowest values of modulus of elasticity, however, with good superficial cohesion. Adding quicklime or a small amount of white cement to the slaked air lime mortar (A+Q30% and C:A, respectively) generally improve the lime mortars characteristics. Nonetheless, a low adhesion to the substrate is observed on the A+Q30% mortars composition. However, the rupture pattern of these mortars is mainly cohesive on the 1st render coat, which means that it is not an adhesion problem, thus the carbonation process is expected to increase their performance. C:A:L5, especially with pigment, presents high values of the dynamic modulus of elasticity. In general, for the same mortar compositions, the use of 5% of fine limestone sand (L5) enhances the performance, when compared to the 10% (L10). Moreover, the addition of inorganic natural pigment did not produce any visible surface cracking and increased the modulus of the elasticity; however, slight whitish stains were visible at the exterior surface and a small reduction of superficial cohesion was indicated by the Durometer hardness value. Concerning the water behaviour, the Karsten tubes test revealed high permeability of all the tested renders, probably due to a low degree of carbonation. The tests carried out in experimental panels seem to point out that the solution of slaked air lime with 30% quicklime and using 5% of fine limestone sand (A+Q30%:L5), at volumetric ratio of (1:0.3):(2.5:0.1), presents the most balanced performance, with good superficial cohesion, moderate deformability allowing to accommodate stresses that might occur within the substrate without failing, and also a balanced water behavior for this case study. Furthermore, it is the composition closest to the original formulation, both in composition and properties.

4. Design specifications and final application

The first step of the rehabilitation process was the consolidation of the structure of the building and the removal of the mortars applied in previous rehabilitation processes, followed by the cleaning of masonry, the repair of infiltrations, the improvement of a natural ventilation system, the introduction

2 Santos et al. 2023.
3 Santos et al. 2025.
4 Veiga and Aguiar 1996.

Figure 1. (a)Experimental applications in situ; (b) Paimogo Fort, after the rehabilitation, in 2024.

of new windows and doors in the existing openings to improve the thermal comfort of the building. The recovery of mortars on the exterior and interior walls was based on the experience previously described, which led to the choice of the mortar with the more balanced performance: (A+Q30%:L5), at volumetric ratio of (1:0.3):(2.5:0.1). The chromatic aspect was also carefully evaluated for what concerns the exterior walls, leading to the application of an inorganic natural pigment, rich in Fe2O, at a concentration of 2% of lime weight, diluted in the mixing water, which gave to the mortar a pale rose tone (Figure 1b). A local stone (Cezaredas limestone) was chosen to complement the floor in the forecourt in front of the building and the water drain channels, for the main doorjambs and architraves, and for the reconstruction of the watchtowers.

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Development of new strategies for the conservation of natural pozzolanic mortars using metakaolin, nano-silica and silica fume

1. Introduction

The integration of pozzolanic materials into ancient Roman mortar mixtures marks a pinnacle of engineering innovation, pivotal in revolutionizing construction practices across the empire[1]. Volcanic sand, readily sourced from the geologically rich environs of Italy, particularly near Mt. Vesuvius, were integral to the Roman architectural success story. The volcano's abundant eruptions provided a wealth of materials, such as volcanic ash and sand, which were harnessed to produce mortars with hydraulic properties. These mortars not only set and hardened in wet conditions[2] but also supported the construction of enduring monuments and infrastructure. The resilience and longevity of structures utilizing natural pozzolanic mortars can be attributed to the chemical interactions between the hydrated lime and volcanic byproducts. These interactions foster the formation of calcium silicate hydrates[3]; compounds renowned for their stability and resistance to environmental aggressors. This pozzolanic reaction was a cornerstone of Roman material technology, giving end-products with enhanced mechanical strength and durability, allowing their architecture to withstand the rigors of time, including factors like water infiltration, thermal cycles, and seismic forces. The strategic application of these materials underscored a profound understanding of geo-resources, enabling the Romans to optimize the structural durability and functional longevity of their constructions. By studying these ancient techniques, we gain invaluable insights into sustainable material use and architectural resilience, guiding contemporary efforts in historical conservation and modern building practices. This legacy not only celebrates Roman ingenuity but also serves as a foundation for advancing current approaches to durable and sustainable construction.

2. Research Aims

Despite their proven durability, natural pozzolanic mortars are susceptible to environmental degradation, which is exacerbated by their intrinsic material properties such as porosity, and their mineralogical and chemical composition. This interaction with the environment highlights the need for meticulously planned conservation strategies, emphasizing the need for a detailed historical and scientific understanding of the original materials before any intervention is undertaken on historical structures[4]. Inadequate restoration practices can lead to irreversible damage, making it imperative to ensure that any new mortars used in the restoration process are fully compatible with the original materials[5]. This compatibility must encompass several key aspects: chemical alignment, physical compatibility and mechanical suitability[6].

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1 Collepardi et al. 2003.
2 Moropolou, Bakolas, Bisbikou 2000.
3 Jackson et al. 2014.
4 Spadavecchia et al. 2024.
5 Collepardi 1990.
6 Venice Charter 1964.

This study aims to address these challenges by developing innovative, compatible mortar mixtures that preserve the structural and aesthetic integrity of heritage buildings constructed with Somma-Vesuvius based pozzolanic mortars. Additionally, with the original volcanic materials becoming scarce, this research will explore alternative sustainable admixtures that can replicate the historical properties of traditional pozzolana. These new mixtures are intended not only to match the original materials in terms of appearance and texture but also to provide enhanced durability and resilience to environmental pressures, thereby reducing the frequency of maintenance and improving the long-term preservation of our architectural heritage.

3. Materials and Methods

The binder used for the mortar renders is a seasoned slaked lime, supplied by CTS srl (Europe), and commonly used in restoration efforts. This material, adhering to standard[7] and classified as CL90-S PL, is predominantly composed of calcium hydroxide (>97% CaO) with a minor inclusion of magnesium oxide (ca. 2%). It features a semi-solid consistency, with a density of 1.3 kg/L and a solid-to-water ratio of 40:60. To authentically replicate Roman pozzolanic mortars, three distinct volcanic aggregates were sourced from an ancient quarry located on the Somma-Vesuvius volcanic complex near Alveo Pollena (Naples, Italy). These aggregates are derived from pumices corresponding to different historic eruptions: Avellino (ca 4000 years ago), Pompei (79 AD), and Pollena (472 AD). Prior to their inclusion in the reference mixtures, these volcanic aggregates were meticulously milled and sieved to a maximum grain size of 2 mm. For the experimental mixtures, a CEN Standard[8] Sand with particle size under 2 mm, supplied by NormenSand (Germany), was used. Additionally, three pozzolanic additives were incorporated into the study to evaluate their efficacy: Metakaolin (Metaver N, supplied by NewChem), Nano-Silica (Aerosil 200, provided by Evonik), and Silica Fume (Sprayset SF, supplied by Fosroc). The mixtures shown in Table 1 were formulated and prepared in the laboratories at the University of Navarra, adhering to ancient recipes from historical literature as Vitruvius' De Architectura (vol. 7). The dry raw materials, comprising aggregate and pozzolanic additives, were mixed for 5 minutes using a BL-8-CA solid mixer (Lleal S.A.) Subsequently, the required amount of water was gradually added to achieve a predefined workability of 160±5 mm on the flow table test[9]. The fresh mixtures were then casted into cylindrical moulds, each 40 mm in diameter and 36 mm in height, and stored for 7 days in curing chamber (RH>95%). After this initial curing phase, the moulds were transferred for curing under laboratory conditions (T=20°C, RH=60%). The properties of the hardened samples are evaluated after 28 days of curing. To ensure the reliability and representativeness of the results, three samples per mixture and curing time are analysed. Once the hardened state is achieved, the samples will undergo extensive analytical assessments to evaluate their physical and mechanical properties. Initial characterization involves techniques such as Particle Size Determination by Laser Diffraction, X-Ray Powder Diffraction, Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy, Thermogravimetric Analysis and Mercury Intrusion Porosimetry. Further test will evaluate the compressive strength, open porosity and apparent density, water absorption coefficient, as well as resistance to salt crystallization and freeze-thaw cycles at intervals of 28, 90 and 180 days of curing.

	REF-A79	REF-472	MK-1	NS-1	SF-1
Hydrated Lime	1	1	1	1	1
Volcanic Aggregate	3	3	-	-	-
Silica Sand	-	-	3	3	3
Additive	-	-	5%	5%	5%

Table 1. Mix design of the five mortar mixtures, values displayed are expressed in volume. Additives were calculated on the binder.

7 UNI EN ISO 9001:2015.
8 EN 196-1:2016.
9 EN 1015-3:2000.

4. Results

A complete characterization of the mortars was carried out through the aforementioned techniques. Values of the compressive strength were obtained and correlated with the mineralogical and chemical composition of the mixes, and the effect of the pozzolanic additions was also ascertained. Some of the samples are currently being studied and their future analysis are expected to shed light on the impacts of varying additives and aggregate types on the mortar's properties, such as strength, durability, and environmental resilience. Detailed findings from this study will be presented at the subsequent conference session, where we will discuss the implications of our results for the conservation of historic structures.

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Enhancing the Properties of Lime Mortars with Volcanic Ash and Hemp Shiv: A Sustainable Approach for Restoration Applications

1. Introduction

Lime mortars, one of the oldest building materials utilized since ancient civilizations, are widely preferred in restoration due to their compatibility with heritage buildings, carbon-negative characteristics, and inherit sustainability[1]. However, traditional lime mortars exhibit drawbacks such as low mechanical strength, prolonged setting times, and slow strength development, which can limit their practical applications. To address these limitations, hydraulic properties of lime mortars have often been enhanced through the addition of pozzolanic materials or by employing hydraulic lime[2]. Additionally, natural reinforcements like hemp shiv have been incorporated to improve mechanical strength and durability.

Hemp is a natural, fast-growing, biodegradable resource, making it highly suitable for sustainable construction applications. Although hemp fibres are commonly recognized for their reinforcing properties and thermal inertia, the hemp shiv, constituting the majority of the plant, often remains underutilized. Hemp shiv possesses potential as both filler and reinforcement in lime-based mortars, contributing positively to their workability, durability, thermal efficiency, and environmental sustainability, making its use in restoration applications particularly promising[3].

This study aims to investigate the effects of volcanic ash and hemp shiv additions on the fresh and hardened properties of air lime and natural hydraulic lime mortars, highlighting their suitability for sustainable and heritage-compatible restoration applications.

2. Materials and Methods

2.1 Materials

Mixtures were prepared using natural hydraulic lime (NHL-5) and calcitic air lime (CL-90) as binders, standard silica sand as aggregate, volcanic ash as pozzolanic agent, and hemp shiv in small proportions as reinforcement (Table 1, Figure 1a). A superplasticizer (SP) based on polycarboxylated ethers was used when necessary to ensure workability.

All dry materials for each mix were initially blended thoroughly to ensure homogeneity. Subsequently, water was added, and the mixture was stirred at a low speed for 90 seconds to attain a uniform consistency. Fresh mortar samples were cast into cylindrical moulds. Air lime mortars were cured under controlled laboratory conditions (20°C ± 2°C, 45% ± 5% RH), while NHL mortars were cured in a curing chamber (20°C ± 2°C, 95% ± 5% RH).

1 Athira and Manohar 2023.
2 Silva, Ferreira Pinto, Gomes 2014.
3 de Bruijn 2009.

2.2 Experimental Methods

The characterization of fresh and hardened mortar samples was conducted according to relevant standards. Fresh state analyses included assessments of fluidity[4], water retention[5], and setting time[6]. Compressive strength measurements were performed at 7, 28, and 91 days. At the end of 91 days, porosity and pore size distribution were evaluated using Mercury Intrusion Porosimetry (MIP) with pressures ranging from 0.0015 to 207 MPa. Thermogravimetric Analysis (TGA) was conducted from 35°C to 1000°C under a nitrogen atmosphere to evaluate the hydration and carbonation processes. Finally, microstructural features were examined using Scanning Electron Microscopy (SEM), with samples prepared by gold-coating to ensure optimal imaging conditions.

	NHL	CL	Silica Sand	Volcanic Ash	Hemp Shiv	SP (%)	Water/ Dry mix	Flow Table (mm)	Setting Time (min)	Water Retention (%)	Compressive Strength (MPa)			Weight Loss (%)	
											7th day	28th day	91st day	200-600°C	600-900°C
N1	1	-	3	-	-	0	0,15	179	259	88,9	1.3 ± 0.1	3.1 ± 0.4	5.8 ± 1.1	3,24	5,69
N2	1	-	3	0,2	-	0	0,15	170	201	88,4	1.2 ± 0.1	3.7 ± 0.5	7.7 ± 0.4	2,41	4,25
N3	1	-	3	0,2	0,01	0,05	0,15	177	189	88,9	1.3 ± 0.1	2.0 ± 0.2	5.9 ± 0.6	2,3	4,47
A1	-	1	3	-	-	0	0,25	201	1431	91,8	0.4 ± 0.01	0.4 ± 0.1	1.0 ± 0.1	3,45	12,94
A2	-	1	3	0,3	-	0	0,25	202	1254	91,4	0.4 ± 0.02	0.4 ± 0.04	0.8 ± 0.02	2,47	9,19
A3	-	1	3	0,3	0,01	0	0,25	201	1457	92,7	0.1 ± 0.04	0.3 ± 0.1	0.7 ± 0.1	2,07	4,25

Table 1. Mix design of the five mortar mixtures. Values displayed are expressed in volume.

3. Results

Fresh state analyses demonstrated that binder type significantly influenced mortar properties (Table 1). Air lime-based mixtures required more water to achieve optimal consistency, compared to natural hydraulic lime mixtures. Additionally, air lime-based mortars exhibited notably longer setting times but demonstrated superior water retention compared to NHL-based mortars. The addition of volcanic ash and hemp shiv reduced fluidity in NHL mixtures; however, these additives did not significantly affect with the fluidity of air lime-based mixtures. Notably, the inclusion of volcanic ash shortened the setting times for both binder types.

Compressive strength results are presented in Table 1. All mortar samples demonstrated an increase in compressive strength over time. In NHL-based mortars, volcanic ash significantly improved strength development, particularly after 28 days. However, the introduction of hemp shiv in sample N3 neglected this enhancement, resulting in strength values comparable to the NHL reference mortar (N1). Among air lime-based mortars, the reference mortar (A1) exhibited the highest compressive strength. The incorporation of volcanic ash and hemp in samples A2 and A3 increased porosity (32.9% and 34.75%, respectively), accounting for the mechanical strength drop. Porosity measurements revealed no significant variations among NHL-based mortars (21.65–22.07%). Nevertheless, SEM analysis highlighted discontinuities at the interface between hemp shiv particles and the binder matrix, indicating potential weak zones affecting mechanical performance (Figure 1b).

Thermogravimetric analysis (TGA) indicated reductions in weight loss for mixtures containing volcanic ash and hemp shiv (Table 1). The decreased dehydration-related weight loss between 200–600°C can be attributed to the pozzolanic reaction between volcanic ash and lime, consuming hydration products. Consequently, carbonation-related weight loss between 600-900°C also decreased. The inherit high-water absorption capacity of hemp shiv may have reduced the availability of free water within mortar matrix, potentially limiting hydration phase formation.

4 UNE-EN 1015-3.
5 UNE-EN 83816:2021.
6 UNE-EN 1015-9:2000.

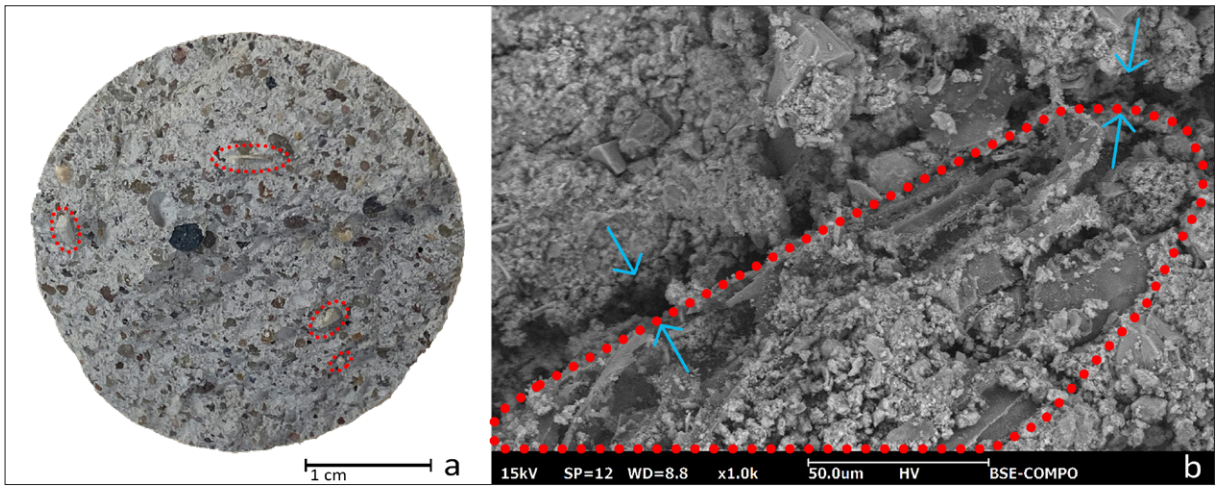

Figure 1. (a) Macro photograph of sample N3, with red dashed lines highlighting hemp shives; (b) SEM image of sample N3 showing hemp shiv (outlined in red dashed lines) and interface discontinuities between the lime binder and hemp shiv (indicated by blue arrows)

4. Conclusions

This study investigated the effects of volcanic ash and hemp shiv on the performance of lime-based mortars. The inclusion of volcanic ash enhanced the compressive strength of NHL-based mortars; however, the simultaneous incorporation of hemp shiv increased porosity, offsetting these strength improvements. For air lime-based mortars, the addition of volcanic ash and hemp shiv resulted in elevated porosity levels and reduced strength development. To build on these findings, future research should explore flexural strength, durability and thermal properties, providing a comprehensive understanding to the performance and sustainability of lime-based mortars.

5. Acknowledgements

This research was funded by Ministerio de Ciencia e Innovación (PID2020-119975RB-I00 LIMORTHER) and EU HORIZON-CL5-2022-D4-02 (101123293-SINCERE). Elif Çam received a fellowship through the Study Abroad Program of the Ministry of National Education of the Republic of Türkiye.

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Experimental Investigation of Compressed Lime-based Bricks

1. Introduction

Bricks are among the most common building materials, used for the construction of walls, pavements etc. Every year, around 1500 billion bricks are produced globally. Mudbricks were the first bricks to be produced, formed from clay and dried in sun. The use of fired bricks started around 5000 BC and since then their production has advanced to fit the modern construction demands. Other types of bricks include i) concrete bricks – a mixture of cement, water and sand – ii) fly ash bricks, an alternative to concrete bricks where fly ash is also added in the mix and iii) calcium silicate bricks which are made from sand and lime[1]. Calcium silicate or sand-lime bricks are a combination of sand (90%), lime (8%) and fly ash (2%). The materials are mixed and molded using a hydraulic press at a pressure around 30-65 N/mm^2. Afterwards, the bricks are kept in an autoclave at a high temperature for up to 12 hours . In this work, an alternative to sand-lime bricks is investigated based on air lime-based mortar composition. Bricks based on hydrated lime were produced and kept in different curing environments (ambient and 3% CO2). The specimens were tested on 28 and 90 days to determine their mechanical, physical and durability properties. The aim of this work is the development of a product that can absorb carbon emissions during its production stage.

2. Laboratory production of compressed lime-based bricks

The experimental investigation is divided in two stages. In the first stage, six mixtures were produced. In each mixture, air lime (CL90) was used combined with different binders such as: natural pozzolan and a by-product of the production of perlite. River sand (0-2) mm, (0-4) mm and recycled marble (0.7-2.0) mm were used as aggregates. A low water/binder ratio was selected for the mix to be compacted and demoulded immediately.

After mixing the ingredients for about 2min, the mortar was poured in a custom-made mould, shown in Figure 1, that was designed to produce compressed earth-blocks. The lime-based bricks were compressed to a hydraulic machine pressure of 1.5-2.0 N/mm2 for each brick. The final dimensions of the compressed bricks were (190x90x40) mm. After compression, the bricks were demoulded and kept at different conditions. Mixtures A1 to A4 - with hydrated lime - were kept at 21o C and RH60%. A5-A6 were kept at 21o C and RH95%. In the second stage, Mixtures A3 and A6 were selected and replicated with the addition of hemp fibres (1% by volume of the mixture). The bricks were shaped according to the same process described in stage 1. After demoulding, they were kept at a chamber with 21o C and 3% CO2 for 28 days. The composition of the bricks is given in Table 1.

After 28 days, the homogeneity of the bricks was evaluated using an ultrasonic pulse device. The compressive strength, density and porosity of the samples were tested at 28 and 90 days. Moreover, the durability of the specimens was determined under freeze-thaw and wet-dry cycles.

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1 Anant 2018.
2 Barbosa 2022.

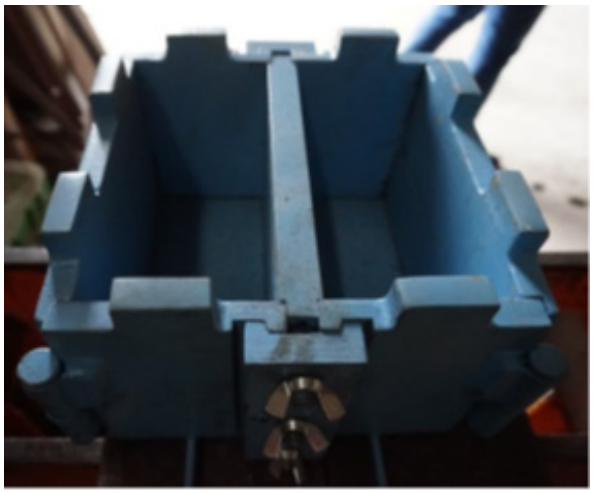

Figure 1. (a) Custom-made mould for compressed bricks (b) Produced lime-based brick (190x90x40) mm

Mix	Binders			Aggregates				Hemp fibres	Water/ Binder	Curing at 3% CO_2
	Hydrated lime	Natural pozzolan	Perlite by-product	River sand (0-4) mm	River sand (0-2) mm	Recycled marble (0.7-1.3) mm	Recycled marble (1.3-2.0) mm			
1st stage										
A1	1	-	-	2	-	-	-	-	0.34	no
A2	1	-	-	-	2	-	-	-	0.34	no
A3	1	-	-	-	2	-	-	-	0.34	no
A4	1	-	-	-	-	1.4	0.6	-	0.34	no
A5	0.5	-	0.5	-	2	-	-	-	0.3	no
A6	0.5	0.5	-	-	1.4	-	0.6	-	0.3	no
2nd stage										
A6e	0.5	0.5	-	-	1.4	-	0.6	-	0.3	yes
A6he	0.5	0.5	-	-	1.4	-	0.6	1%	0.3	yes
A3he	1	-	-	-	2	-	-	1%	0.34	yes

Table 1. Composition of lime-based bricks (parts per weight)

3. Conclusions

Based on the evaluation of the overall performance of the samples, it can be concluded that bricks based on lime can be produced with good mechanical properties and good durability. The density of the bricks varied from 1500 to 1700 (kg/m3). When maturing took place at ambient conditions, bricks with hydrated lime in combination with natural pozzolan (A6) reached 5.37 MPa under compression at 28 days. Bricks containing only hydrated lime as a binder and hemp fibres achieved 8.30 MPa when curing occurs at 3% CO2 (A3he). The results are given in Figure 2.

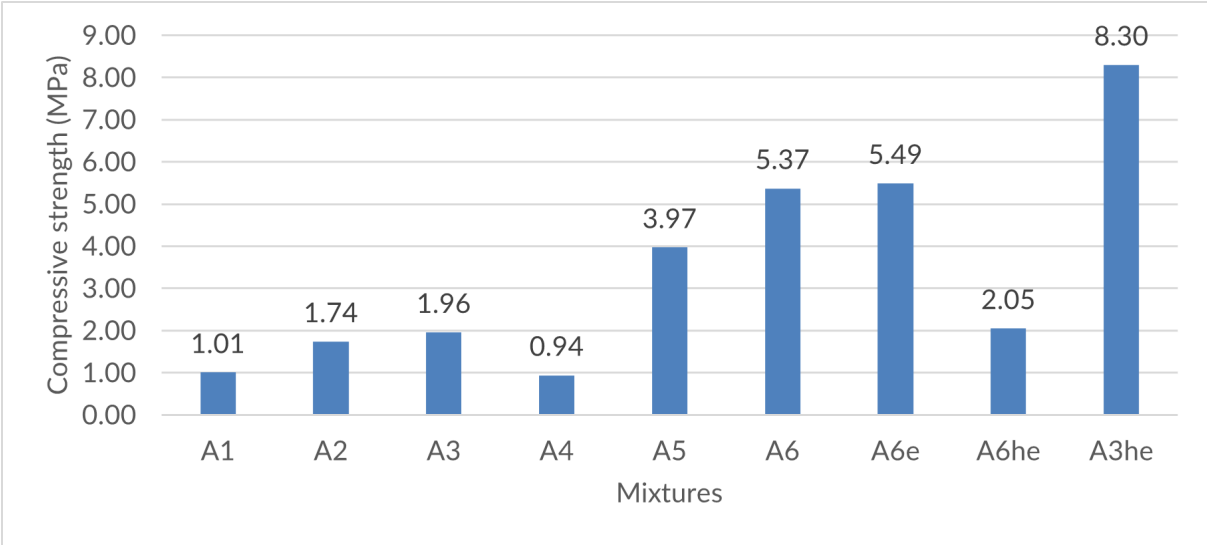

Figure 2. Compressive strength of the lime-based bricks at 28 days

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Revitalizing gypsum mortar for restoration purposes in Koya (Kurdistan-Iraq)

1. Introduction

This paper will present the results of an experimental but scientifically accompanied project in Kurdistan-Iraq to revitalize the production of gypsum setting-mortar for monument compliant restoration purposes, which took place in 2024.

Before the general availability of cement, for centuries gypsum served as setting mortar and plaster in historic buildings in Koya (Kurdistan-Iraq) instead of lime. Locally available and easy to work with, it was the most popular mortar in this hot region.

In the area, north and northeast of Koya, there are still several quarries where a particular type of gypsum rock, which in the past provided the stone material for setting mortar. The burning of gypsum was one of the very special and unique regional building crafts that is in the process of being lost due to the widespread use of cement, even though high quality gypsum mortar is desperately needed for preservation and monument compliant restoration projects.

During the execution of the emergency safeguard measures in the most significant historic building in Koya (Mahmud Agha Khan), we observed that the masonry technique used by the local masons was clearly adapted to the fast-setting gypsum mortars. The resulting masonry with the light gypsum mortars appears to be a construction technique optimized for this region with its hot climate (causing problems with the use of lime mortars - especially the intensive finishing and the 'risk of 'burning') and the probability of earthquakes.

A laboratory mortar analysis carried out on a historic mortar sample showed that the historic mortar used at the Mahmud Agha Khan was of a quality that cannot be reached by the industrial produced gypsum available in the region today.

2. The Project: Implementing Challenges and Results

To address the need of high quality gypsum mortar for restoration purposes, in 2024 a project was launched with funding of the German Gerda-Henkel-Foundation to approach scientifically and experimentally the revitalization of high-fired gypsum mortar as setting mortar for monument compliant restoration. This included the laboratory analysis of the region's stone material (microscopic examination of thin sections and thermogravimetry) and historic mortar samples taken from the 19th century Mahmud Agha Khan (compressive and flexural strength).

For the reactivation of the traditional processing a ruined kiln was repaired. The gypsum stones were extracted from a disused quarry next to the kiln. Three firing processes were carried out under slightly different conditions concerning heat and burning duration. Also in the grinding process different seizes of sieves were used to gain experience with controlling the grading curve.

To observe the suitability of the obtained gypsum mortar a test restoration (completion of a partly collapsed wall) was implemented in of one of the historic buildings in the old town of Koya. In addition, the results were laboratory tested over a period of six months including weathering cycles. The tests included compressive strength, flexural strength (see table 1, results) and ultra sound.

Figure 1. Grinding of the newly burned stones. Stones ready for grinding are collected in buckets in front of the kiln to the left and carried to the grinding mill.

Revitalizing Historic Gypsum Production in Koya						
Sample	**Compressive Strength (Mpa - Nmm2)**	**Flexural Strength (Mpa - n/mm2)**		**Sample**	**Compressive Strength (Mpa - Nmm2)**	**Flexural Strength (Mpa - n/mm2)**
Historic Mortar				New Mortar 1st and 2nd Charge		
University of Prague (2022)				**University of Koya (2024**		
Khan 2		1,8		Sample 1A	5,1	1,5
Khan 4		2,1		Sample 1B	4,7	
				Sample 1C	5,2	
Dr. Azad Saeed (2024)				Sample 2A	5,6	1,9
GM 1 Corner Room	3,9			Sample 2B	4,2	
GM 2 West Arcade	3,4			Sample 2C	5,3	
				Sample 3		1,7
				FEAD (Berlin/Germany) 2024		
FEAD (Berlin/ Germany) 2024				Sample 1	6,3 / 5,6	2,6
20 West Arcade	11,8			Sample 2 (after 6 months weathering)	7,9 / 8,9	4
21 West Arcade	8,9			Sample 3 (after 6 months weathering)	9,4 / 9,0	5,9
22a West Arcade		4,4		Sample 4	6,,3 / 6,2	3
23a Corner Room	10,9			Sample 5	3,3 / 3,4	2,8
23b Corner Room	10,8			Sample 6	3,6 / 4,0	4,6

Table 1. Results of the tests of the historic and newly produced mortars (flexural and compressive strength)

The process was documented in detail in order to promote the rehabilitation of this building craft, which has almost been forgotten, and to enable quality assurance in the re-creation process.

3. Conclusion

The lecture will reflect on the results on different levels of this project: First, the geological components of the regional stone material according to the petrographic analysis. Second, the comparison of the scientific results of the historic and new mortars including the impact of weathering cycle of six months. Third, the challenges we faced on-site while revitalizing this almost forgotten traditional craft. This including the preparation of the kiln, the revitalization of a grinding mill with appropriate sieves to achieve the desires grain mixtures as well the only orally preserved knowledge on the burning process itself.

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Traditional organic additives for improved gypsum plasters

1. Introduction and objectives

Gypsum (CaSO4·2H2O)-based plasters and mortars have been traditionally used for exterior (Figure 1a) and structural applications[1]. This is in stark contrast to modern gypsum products that are almost exclusively used for indoor finishing purposes[2]. Considering its low calcination temperature and the fact that no CO2 is released during calcination as compared to lime or cement, gypsum holds great potential as a sustainable building material for new construction and conservation interventions. A limiting factor is, however, its low weathering resistance, having a much higher solubility (CaSO4, 2.6 g/L at 25°C) than lime-based binders (CaCO3, 0.013 g/L at 25°C). Historically, countless organic and inorganic additives such as lime, oils and animal fats, resins, wax, casein, starch, and animal glues have been added to mortars and plasters in order to improve their durability[3]. Numerous sources cite soap as an additive or surface treatment in order to improve the wet-chemical resistance of lime-based plasters[4]. However, this approach has rarely been considered for gypsum-based materials[5]. Traditional soaps are commonly produced using fats and oils mixed with either sodium or potassium hydroxide, which can potentially result in the formation of harmful sodium or potassium carbonates. Here, the effectiveness of a calcium soap formed upon reaction of vegetable oil and limewater is evaluated as an alternative additive for gypsum plaster that would avoid the formation of harmful salts. The performance of plasters containing soap is compared to plaster samples prepared with either water or limewater. The outcome of the study has important implications for the design of optimized gypsum plasters for exterior application in conservation interventions and new construction.

2. Materials and Method

Small-scale prismatic (1x1x4 cm) and cylindrical (2.5x0.5 cm) plaster samples with a 0.9 water/solid ratio (wt/wt) were prepared and evaluated using an array of analysis (X-ray diffraction (XRD) and contact angle analysis (CA)) and tests (flexural and compressive strength, water vapor transmission, and weathering resistance using water spraying). The raw materials include reagent grade gypsum and calcium hydroxide (Sigma-Aldrich) as well as vegetable oil (Table 1). Gypsum was calcined at low180 and high T330 °C to mimic modern industrial or traditional calcination conditions, respectively, and mixed with distilled water (W) or saturated limewater (LW) with or without the addition of 1 and 5 wt% oil (considering the gypsum dry weight). Samples were cured for 7 days at 95% RH to ensure complete hydration and afterwards stored under laboratory conditions for 21 days before testing.

1 Bel-Anzué, Elert 2021.
2 Middendorf 2002.
3 Garate Rojas 1999.
4 Bossert 1950; Díaz Macías 2019.
5 Risdonne 2021.

Sample	Gypsum	Oil	Water/Lime Water	Liquid/Solid Ratio
180-W	100	0	90	0.9
330-W	100	0	90	0.9
180-LW	100	0	90	0.9
330-LW	100	0	90	0.9
180-LW-1oil	100	1	89	0.9
330-LW-5oil	100	1	89	0.9
180-LW-1oil	100	5	85	0.9
330-LW-5oil	100	5	85	0.9

Table 1. Composition of gypsum plaster (g)

3. Results and Discussion

A hydration study performed using continuous XRD analysis of fresh plaster samples showed delayed hydration of samples prepared with limewater, the presence of oil leading to further delay. Contact angle measurements revealed no important differences among samples prepared with either distilled water or saturated limewater, all samples being extremely hydrophilic. The contact angle and the time required for the complete absorption of a 4-µL water drop, in contrast, increased significantly in the case of all samples containing soap (formed upon reaction of the oil and the limewater), samples containing 5 wt% oil even reaching contact angle values in the hydrophobic regime. Remarkably, samples prepared with gypsum calcined at high T were slightly less hydrophilic independent of kneading water composition. None of the additives, in contrast, had a significant effect on the plasters´ water permeability and observed differences were within error. According to the weathering test results (Figure 1b), the addition of limewater had a negative effect on the plasters´ durability, which was, however, in some cases offset by the presence of soap. Generally, plasters prepared with gypsum calcined at high T revealed slightly better weathering resistance as compared to their counterparts prepared with gypsum calcined at low T. The addition of limewater with or without oil led to a strength decrease, yet plasters still complied with the established minimum requirement of 2 MPa (AENOR). Remarkably, limewater and soap had a positive effect on flexural strength in most cases and values were within the reported range for pure gypsum plaster of 3.6-8 MPa[6]. The outcome of this study indicates that it is feasible to design water repellent gypsum plasters and control their hydration time using calcium soaps as additives. The obtained plasters

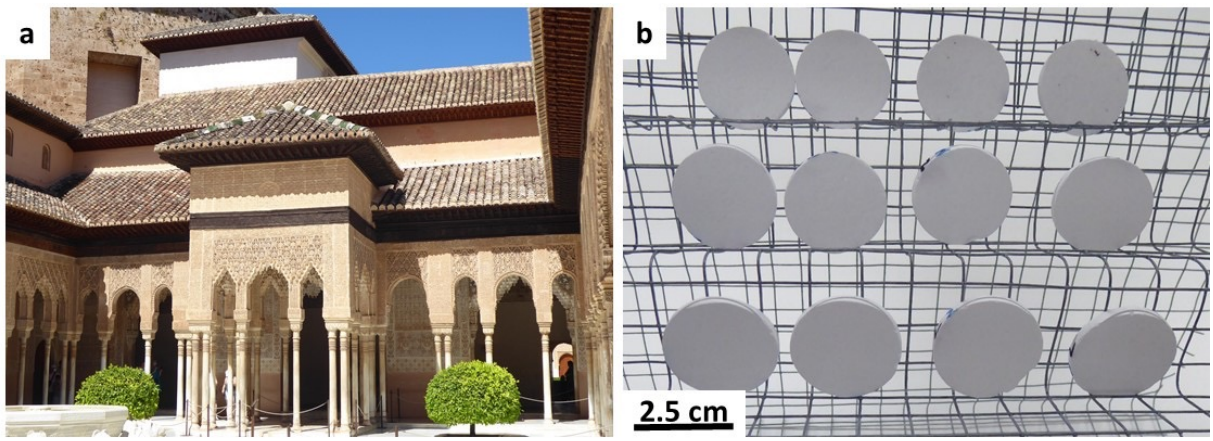

Figure 1. a) Outdoor-exposed gypsum plasterwork (yesería) at the Alhambra fortress (Spain), b) plaster samples subjected to water spraying during a non-conventional weathering test.

6 Elert et al. 2023.

have sufficient strength for most finishing purposes and present a sustainable alternative to conventional plasters for conservation interventions and new construction.

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Structural gypsum mortars in Iran: from history to sustainable architecture

1. Motivation

The architectural legacy of the Persian region is inextricably linked to its abundant gypsum deposits, a resource that has profoundly shaped building practices for millennia. Historically, gypsum was not merely a decorative element but a vital structural material, particularly when processed into durable mortars. These mortars played a crucial role in the construction of robust and enduring structures, demonstrating gypsum's inherent strength and versatility. While contemporary applications of gypsum in architecture often prioritize its aesthetic qualities and fire-resistant properties, there is a growing recognition of its potential within the context of sustainable construction. In an era where the imperative for low-energy materials and circular economy principles is increasingly urgent, a comprehensive reevaluation of gypsum's structural capabilities becomes essential. This paper seeks to elucidate the significant influence of traditional gypsum structural mortars on the evolution of Persian architecture, exploring the techniques and applications that allowed for its effective utilization. Drawing on documented historical examples, particularly from the Sasanian period onward, the study highlights the proven structural use of gypsum in arches, vaults, and ribs. Furthermore, it aims to bridge the gap between historical precedent and contemporary practice, demonstrating how the knowledge gleaned from traditional gypsum mortar applications can be successfully integrated into modern architectural designs that prioritize environmental sustainability and resource efficiency. By highlighting the structural potential of gypsum, this study endeavors to contribute to a broader discourse on the use of locally sourced, sustainable materials in contemporary architecture, offering a valuable perspective on the enduring relevance of traditional building practices in addressing modern environmental challenges.

2. Historical Development: A Chronological Exploration

Gypsum, a low-energy processing material, predates lime in construction. Its strength and binding capacity, due to its crystalline microstructure after hydration, were recognized in antiquity. Evidence of gypsum concrete appears in 14th c. BCE Tell El-Amarna, Egypt. Gypsum mortars were used in brick construction from the 26th c. BCE Indus Valley (Mohenjo-Daro, Pakistan) to Elamite (16th c. BCE, Iran), Assyrian (912-605 BCE, Iraq), Parthian (c. 247 BCE - 224 CE, Iran/Iraq), and Sasanian (224-651 CE, Iran) architecture, notably in royal tombs and palaces. This tradition continued into early Islamic construction, as seen in 9th-10th c. CE Uzbekistan (Samarkand)[1].

The rapid setting of gypsum and volume increase during hardening were crucial for vaulted construction. Techniques developed from the 1st to 13th c. CE, leveraging gypsum's adhesive properties, allowed for innovations like pitched-brick arches. Early examples exist in 14th c. BCE Iran's Tepti Aharos Vaulted tomb () and 1st-2nd c. CE Iraq's Pillared Hall of Ashur. Sasanian architecture furthered this, using fibre-reinforced gypsum arches for both temporary and permanent structures, as seen in 2nd c. CE Neisar, Iran. These arches were typically reinforced with bundled reeds, while the gypsum mortar was often modified

1 Kingery et al. 1988, Vitti 2024.

with local additives; such as clay, sugar, animal hair, or fruit-based liquids, to enhance workability and durability. These techniques influenced Umayyad (661-750 CE, Syria/Jordan) and Abbasid (750-1258 CE, Iraq) architecture, including Amman Citadel (Jordan) and Al-Ukhaidir Fortress (Iraq). The evolution of gypsum use facilitated the development of thin rib vaults, culminating in impressive Persian rib vaulting from the 10th-12th c. CE (Iran). The fast-setting gypsum mortar allowed for rough execution, highlighting its practical advantage[2].

3. Data Presentation

Recent archaeometric studies on historic structural gypsum mortars are significantly advancing our understanding of gypsum deposit utilization, historic production techniques, and firing processes, ultimately illuminating the chemical, physical, and mechanical properties of these crucial materials[3]. These studies reveal the sophisticated strategies employed by ancient builders to enhance mortar durability through careful gypsum selection and refined production recipes. Examples include the analysis of gach-buri, a gypsum-based stucco known for its intricate detailing and longevity and koshteh, a specific type of gypsum plaster used in various architectural applications. Concurrently, ethnographic studies are providing valuable insights into the traditional production methods of gypsum mortars, demonstrating that historic production was often localized, occurring in close proximity to construction sites[4]. This localized production model likely contributed to the development of seminal construction improvements in the southwest region of Iran. It is worth noting that the regions with considerableVast gypsum deposits are located instretch across central, western, northern, and southwestern Iran., with Semnan, Qoum, Yazd, and Khorasan arestanding out as the primaryleading production provinces known. These regions are particularly vital for gypsum production. Due toextraction because of the substantialexceptional thickness of their gypsum beds, these regions are regarded as the most crucial sites for gypsum occurrences. For instance, the proximity of ancient architectural centers to these high-quality gypsum sources facilitated the widespread use of gypsum in vaulted construction, leading to architectural innovations that endure to this day. Specifically, ancient sites such as Neisar (Kashan, Central Iran) demonstrate sophisticated use of gypsum vaults. These sites, located within a relatively short distance of major gypsum quarries, show a direct correlation between material availability and architectural technique. An element that significantly improved the structural efficiency of gypsum, making it possible to use it in the vaults, was the addition of fibers, particularly for the construction of ribs.

4. Conclusions

Iran's abundant gypsum reserves establish it as a significant global producer, yet the contemporary building industry largely confines its utilization to plaster, plasterboard, and cement aggregate production. This limited scope overlooks the material's potential for broader structural applications, as evidenced by its historical use. A comprehensive study of historic gypsum mortars, encompassing both archaeometric analyses and an examination of their role in developing innovative construction techniques, holds immense potential for expanding gypsum's applications in modern construction.

Historic structural gypsum mortars exhibitpossess remarkable properties, including: a low-energy production process, rapid setting with excellent adhesive capacityadhesion, inherent fire resistance, and commendable mechanical strength, particularlyespecially when reinforced with natural fibers. These attributes, evidenced by meaningful historical applications, suggest that gypsum could serve gypsum's potential as a sustainable and efficient alternative to conventional construction materials, as some meaningful applications document.. However, a more systematic approach is neededcrucial to bridge the gap between historical practices and contemporary architecture. This approach should focus oninvolves correlating the use of structural gypsum with detailed analyses of construction techniques, highlighting

2 Galdieri 1983, Arce 2003, Lushnikiva, Dvorkin 2016, Memarian, Safaei Pour 2016, Shekofteh, Oudbaschi 2019.
3 Shekofteh, Oudbaschi 2019, Djamali et. al. 2021, Koochakzaei et al. 2023, Hamzavi et al. 2023.
4 Oudbashi, Shekofte 2008.

how the material was adaptedemphasizing its adaptation to meet structural requirements and how it facilitated the evolution ofits role in evolving novel architectural forms and expressions. By thoroughly. Thoroughly documenting and analyzing these historical precedents, we can will unlock thegypsum's full potential of gypsum to contribute tofor sustainable and innovative architectural solutions today and in the present and future. FurtherWhile this study relies on historical documentation and secondary archaeometric analyses rather than original laboratory testing, further research shouldis needed to prioritize the development of standardized testing and application guidelines to facilitate the, thereby facilitating gypsum's integration of gypsum into modern building practices, while ensuring both structural integrity and environmental sustainability.

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Study of pozzolanicity in mortars with diatomaceous earth for restoration

1. Introduction

The conservation of architectural heritage requires the use of materials compatible with historic mortars that can preserve the integrity of ancient constructions while offering durability over time. Lime mortars are widely used in restoration projects due to their porosity, flexibility, and compatibility with historical substrates[1]. In this context, the incorporation of pozzolanic additions in lime mortars has been shown to improve their mechanical properties[2]. Diatomaceous earth has been known as a pozzolanic material since ancient times, used in Greece for construction, as a lightweight material, in the manufacturing of structural ceramics, and as abrasives[3]. In Rome, its use continued, notably in the reconstruction of the dome of the Hagia Sophia in Constantinople in 432 BC, where diatomaceous earth-based bricks were used due to their lightness[4]. Following this line, diatomaceous earth, with its high content of amorphous silica, has proven to enhance the mechanical properties and durability of lime-based mortars[5]. This study investigates the effect of diatomaceous earth from two different mines, one from freshwater in Spain and the other from saltwater in the USA, comparing the influence of their origin in different habitats. Additionally, both raw and calcined diatomaceous earth will be used to compare the different effects when reacting with lime. Furthermore, it will be compared with lime mortars containing metakaolin, which has also been used as part of the study. Diatomaceous earth has been widely studied for various applications, such as filters[6], insecticides[7] and in construction, where it has been used in cement mortars[8], hydraulic lime[9], concrete[10], ceramic materials[11] and in improving the thermal behavior of activated lime mortars[12]. This research in this field. The main objective of this research is to evaluateaims to assess the pozzolanic activity of two types of diatomaceous earthsearth from different habitats,environments combined with air lime, for restoration mortars, and compare them with mortars containing lime and –metakaolin mortars. The study aims to evaluatefocuses on analyzing the physical and chemical properties of the diatomaceous earths in the mortar formulations, investigate the effect of adding diatomaceous earth and metakaolinadditives, evaluating their impact on the mechanical properties of lime mortars, and compare the mechanical behavior and pozzolanic activity of mortars with and without these additives. Additionally, the research aims to exploreperformance, and examining pozzolanic reactions in the mortars through

1 Silva, Ferreira and Gomes 2015.
2 Sepulcre A, 2005.
3 Rodas González et al. 2011.
4 Stoermer and Smol 1999.
5 Loganina et al. 2014.
6 Vasconcelos, Labrincha, and Ferreira 1998.
7 Korunic 2013.
8 Li et al. 2020.
9 Tavares et al. 2016.
10 Posi et al. 2013.
11 Šaponjić et al. 2015.
12 Barbero 2011.

their performance in and long-term durability tests, conduct a detailed analysis of the microstructures and crystalline phases of the mortars using. Advanced techniques such as SEM, XRD, and TGA, are used for microstructural and ultimately applyphase analysis, with the designedfinal goal of applying the developed mortar in a real restoration project.

2. Materiales

The study uses air lime CL-90S according to the standard (UNE-EN 459-1:2016 2016) as the base material for the mortars. Three types of diatomaceous earth are employed:
- Natural diatomaceous earth from Albacete, Spain (DEN).
- Laboratory-calcined diatomaceous earth at 700°C from natural material sourced from Spain. (DEC-1).
- Diatomaceous earth calcined at 1000°C from the USA. (DEC-2).

Additionally, metakaolin (10-20%) is added to some mortars to investigate the combined effect of these materials on pozzolanic activity, as shown in Table 1, which details the mix proportions and mortars produced. Different water-to-cement ratios were studied, and mortars with a 1.2 ratio were ultimately selected due to their similar values in terms of flow diameter.

Mortar	Lime	Metakaolin	Natural Diatomaceous Earth	Calcined Diatomaceous Earth	Sand	Water
CA-1	1	-	-	-	3	1,1
CA-2	1	-	-	-	3	1,2
CADEN20	1	-	0,2	-	3	1,2
CADEC20 -1	1	-	-	0,2	3	1,1
CADEC20 -2	1	-	-	0,2	3	1,2
CADEMB20-1	1	-	-	0,2	3	1,2
CADEMB20-2	1	-	-	0,2	3	1,3
CAMKDEC20	1	0,1	-	0,1	3	1,2
CAMKDEN20	1	0,1	0,1	-	3	1,2
CAMKMB20	1	0,1	-	0,1	3	1,2
CAMK20	1	0,2	-	-	3	1,2

Table 1. Mortar mix proportions

3. Results

Using SEM, XRD, TGA/DSC, and EDX, the diatomaceous earths and resulting lime mortars were characterized. Natural diatomite (DEN) showed high porosity, an amorphous siliceous structure, and the presence of carbonates. Calcination at 700 °C (DEC-1) led to the formation of reactive crystalline phases such as alite and belite. Calcination above 1000 °C (DEC-2) produced cristobalite and tridymite, significantly reducing the material's reactivity. Mortar with DEC-1 (CADEC-1) exhibited a dense matrix, presence of C-S-H type reaction products, and a Ca/Si ratio close to 1 according to EDX analysis. CADEN retained its initial porous structure with low reactivity. CADEC-2 showed signs of surface sintering and minimal interaction with lime. The incorporation of diatomaceous earth promoted pozzolanic reactions with air lime, resulting in the formation of C-S-H type phases responsible for matrix consolidation.

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Sustainable plasters for conservation and bio-architecture: experimental results from the reuse of extractive and agro-industrial waste

1. Introduction

The construction and restoration sectors are increasingly focusing on low-impact materials that combine sustainability, compatibility with historical substrates and efficient performance[1]. In this context, the development of lime-based sustainable plasters - formulated through the reuse of extractive and agro-industrial waste - represents a promising line of research at the intersection of bio-architecture and conservation[2]. This abstract presents the first results of a project developed within the PNRR NODES - Spoke 2 (Progetto Bandiera GRIP), in collaboration with the Scuola Edile di Torino, the company Athena Art and the CNA di Torino.

2. Methods and Materials

The study investigated the use of circular raw materials such as fine-grained ornamental stones processing waste[3], rice husk (Figure 2), and other secondary resources as partial substitutes for tradition-

Figure 1. Sustainable plaster applied on brick table

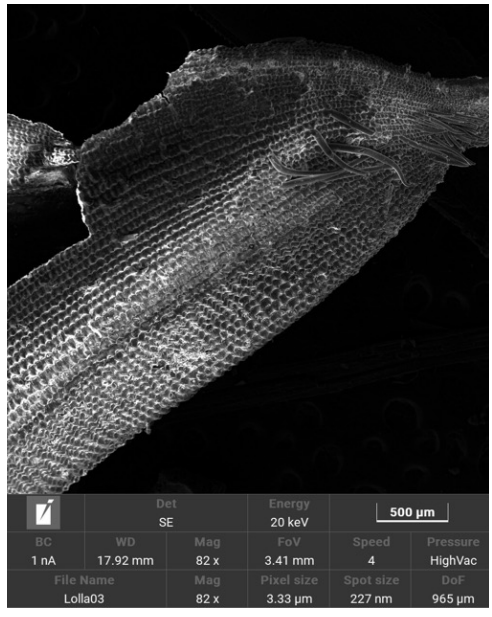

Figure 2. Electron microscope photo of rice husk

1 Schmidt et al. 2019.
2 Michels & Lippi 2020.
3 Tazzini et al. 2024.

al aggregates and/or binders in lime-mortars. The formulations were tested through a wide set of physical-mechanical analyses both in fresh and hardened states (compressive and flexural strength, workability, setting time), alongside tests for water vapour permeability, thermal conductivity, and contact angle. The microstructural and mineralogical characterization was performed using optical microscopy, SEM-EDS, XRD[4]. Also superficial FT-IR spectroscopy was performed. A pilot study was also conducted on a test masonry structure to verify real-life applicability and performance.

3. Preliminary results

The developed materials showed physical and mechanical performances comparable to current bio-based commercial plasters. Results confirm good vapour permeability, adequate strength values and low thermal conductivity, in some mixes. Microstructural analyses highlighted homogeneous matrices with effective integration of secondary raw materials. The combination of performance, compatibility and reduced environmental impact supports the feasibility of these materials for both restoration and new sustainable constructions.

4. Conclusion

This work highlights the potential of sustainable plasters as functional and sustainable solutions for building and heritage conservation. The integration of diagnostic techniques with pilot-scale experimentation has made it possible to validate the materials in both laboratory and field contexts. The collaboration between research institutions, artisan companies, and training centres has enabled a multidisciplinary approach with strong territorial relevance. The research lays the groundwork for further development of sustainable construction materials, with a focus on and circular economy principles. A national patent application has been filed for the formulations developed.

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Sustainability by design: the case of reproduction of Finta Pietra type renders for the National Theatre of Rhodes, Greece

The present study takes the opportunity offered by the design of a context-appropriate restoration rendering mortar for the conservation of the National Theatre in Rhodes to discuss aspects of sustainability and the environmental impact of renovation mortars. Built at the end of the 1930s, the National Theatre of Rhodes (Teatro Giacomo Puccini) serves as an important example of the Italian colonial architectural legacy in the Dodecanese and on the island of Rhodes. Today, this historic building stands as a monument protected under national heritage law for modern architectural heritage and is currently undergoing rehabilitation to address structural integrity issues in the building shell (spalling), which caused the detachment of the original renders, thus necessitating their replacement.

The study is framed around the issue of sustainability as a key criterion in the design, evaluation, and selection of the mortar mix, alongside the notions of authenticity and the requirement for compatibility with the original material.

The study uses the original renders that once clad the reinforced concrete building shell of the National Theatre of Rhodes—the so-called Finta Pietra—as a guiding reference. The first examples of Finta Pietra, a cement-based type of artificial stone (also referred to as faux stone) render mortar designed to mimic the appearance of local sandstone, were introduced on the island of Rhodes during the Italian Occupation (1912–1947), a period that significantly transformed the town's architectural character[1]. The introduction of new building technologies—replacing traditional sandstone structures with concrete and shifting from lime-based binders to cement-based ones—drastically altered the medieval town, shaping a new urban environment.

To understand the composition of the original renders (binder type and aggregate characteristics)—which would in turn guide the design process for a render replacement—samples were examined via stereo-microscopy, optical microscopy and scanning electron microscopy (SEM/EDX) in both fractured surfaces and polished sections, and tested for physical properties using hydrostatic weighing to determine total porosity by calculating their apparent and real densities. The mineralogical composition of binder and aggregates has been determined by X-ray Diffraction (XRD) and Thermogravimetric analysis (DTA/TG). Examination of the original Finta Pietra samples shows that they are preserved in good condition despite having been exposed to an aggressive marine environment for almost a century. The render samples maintain considerable cohesion and strength, with minimal surface wear, in contrast to the reinforced concrete elements, which suffer extensive degradation due to corrosion of their reinforcement. Samples from different façades (external and internal) and heights exhibit similar surface texture and technology, covered with a thin layer of pigmented coating. In terms of their makeup, the samples are composed of the same aggregate, rich in fossils, with a grain size not exceeding 3 mm, while open porosity ranges between 19-25%. The results of these analyses (grain size, porosity, sand composition), together with tests on locally sourced and available aggregates (bulk density, void ratio), informed the reproduction of the original Finta Pietra mixture, with a binder-to-aggregate ratio of 1:2.5 (w/w) and a grain size range of 0–4 mm for pre-washed local crushed sandstone as the chosen aggregate. Since replicating the stone's

1 Kollias 2001.

appearance was a primary objective, the binder-to-water ratio was adjusted to ensure proper workability of the mixture. Workability was determined according to EN 1015-3[2] standard, resulting in a flow table test value of 15 cm.

Moving to the design parameters of restoration mortars, these had to meet the compatibility requirements[3] of the original structure, including technical, functional, and conceptual requirements (i.e., Finta Pietra being a cement-based mortar as defined in the literature)[4]. However, beyond the usual compatibility criteria, this study also assessed the sustainability of the restoration mortar, in terms of the embodied environmental footprint of mortars. In the lab survey for the most appropriate render proposal, three cement-based conservation mortar mixtures were designed and evaluated, using three different cement categories, while keeping the aggregate attributes unchanged for all specimens. For this study, the selected binders belonged to the CEM I, CEM II, and CEM IV cement categories. The latter were chosen because they contain significantly lower amounts of cement clinker: CEM II (B-M) (clinker content 65–79%) and CEM IV (clinker content 65–89%).

The baseline set for the evaluation of different mixtures in terms of performance encompasses aesthetic characteristics and appearance, compressive strength, porosity, and durability against salt crystallization. The key tool for evaluating material sustainability was the Life Cycle Assessment (LCA), which considered not only the energy-intensive production stage of the mortar but also its long-term performance. The durability of a mortar affects the frequency of required maintenance, as well as the need for repair or replacement of the material. Since the LCA consists of three main stages—A, B, and C—this study aimed to assess the material's sustainability across all stages[5]. The focus was particularly directed towards Stage A ("cradle to gate"), which accounts for the high CO_2 emissions during manufacturing, and Stage B, which considers durability and the need for maintenance or replacement. The objective was to identify the most environmentally sustainable mortar mixture while fulfilling conservation requirements and preserving traditional practices. To mitigate the CO_2 emissions associated with cement clinker production, we aimed to reduce its use by incorporating supplementary cementitious materials (SCMs) into the mix. This strategy directly lowers the carbon footprint in Stage A of the LCA. However, achieving true material sustainability also required evaluating performance in Stage B. The more durable the material, the less frequently it requires replacement, ultimately reducing the demand for new material production. To this end, evaluation of Stage B was carried out by comparing the three proposed mortar compositions in terms of their mechanical properties, including flexural and compressive strength, as well as their physical properties, such as porosity and water absorption. Considering the harsh marine environment to which the building is exposed, a durability test was conducted to assess the susceptibility of the mortar compositions to salt-induced damage. This was done through laboratory-accelerated aging against soluble salt crystallization, including chlorides and sulphates, following the standardized procedure (EN 12370)[6].

By developing mortars with enhanced durability suitable for aggressive marine environments, we extend the lifespan of historic structures like the Rhodes National Theatre and reduce resource consumption. Our findings suggest that utilizing cement formulations with reduced clinker content can substantially lower carbon emissions compared to conventional options while maintaining required performance characteristics. Through comprehensive life cycle assessment across production and service stages, this study establishes a pragmatic framework for balancing technical compatibility requirements with environmental considerations, thereby aligning heritage preservation practices with broader environmental sustainability requirements and priorities.

2 EN, 1999.
3 RILEM TC 167-COM, 2005.
4 Fabbri, Rocchi 2014.
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6 EN, 2020.

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Industrial Organic Wastes in Lime Mortars and Sustainability

Increasing industrialization, population growth, and urbanization have led to a surge in research on building materials. Cement, as the most widely consumed building material, poses serious environmental concerns due to high carbon emissions during its production. In contrast, lime-based materials can gain strength by absorbing carbon dioxide from the air, and their performance can be enhanced through the use of additives—an area that has drawn significant attention from both national and international researchers across various disciplines (Corradi et al., 2024; Bengal et al., 2024; Rigopoulos et al., 2021; Basteriz & Menendez, 2020; Benhelal et al., 2021). Moreover, industrial waste generated from production activities has become a growing global concern. The value of recycling such waste, in line with circular economy principles, is increasingly acknowledged across disciplines (World Bank, 2023; Scalia et al., 2021). As a result, the rise in sustainability-oriented studies and growing awareness of recycling and waste management have become inevitable (Nyika & Dinka, 2022). In this context, 'Life Cycle Assessment'—a method that extends beyond modern building materials to include heritage conservation—should be considered in the selection of materials for restoration, encouraging broader sectoral contributions. Recent studies emphasize the use of waste-derived additives, the revival of traditional material practices, and the evaluation of material waste, energy and water consumption, along with the historical, aesthetic, and physical properties of heritage structures and the socio-economic and cultural dynamics of their surroundings—framed under the concept of 'Economy–Environment–Engagement' (Stefanidou et al., 2014; Copsey, 2019; Almeida et al., 2021; Basteriz & Menendez, 2021; Kayan & Forster, 2016; see also Gravagnuolo et al., 2019). This study aims to explore the feasibility of deriving additives from traditional sources—specifically industrial organic wastes such as whey and cotton—in line with contemporary conservation approaches, and to develop a novel, sustainable product that enhances the properties of lime mortars used in restoration. The project aims to disseminate its outcomes to relevant stakeholders from public institutions, the private sector, academia, and international platforms.

Sample groups will be created using both natural hydraulic lime and air lime as binders (whey and cotton)
In sample groups prepared with each binder type, whey and cotton additive will be added to mortar mixtures at 5 different rates (by weight%) and 3 samples with the same additive rate will be prepared.
Whey will be used instead of water in another group.
All prepared samples will be left to cure for 7, 14, 28, 90 days. The tests to be performed on all samples are shared below
Tests planned for carbonation monitoring;
Phenolphthalein Test, XRD, Microscopic examinations in thin sections, SEM-EDS, TG\DTA
28 and 90 days, except for the analyses to be made to monitor carbonation in samples left to daily curing periods,
Tests planned to be performed to determine the pore structure, size and distribution of mortar samples;
Ultrasound Velocity Measurement, Mercury Porosimetry, SEM ImageJ
The analyses mentioned above are still ongoing as part of the study of doctoral thesis. Therefore, the results will be shared on the symposium.

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Development of sustainable pozzolanic binders: combining archaeometry and engineering for the assessment of heritage-inspired geo-materials

1. Introduction

1.1 Pozzolanic binders: calcium vs magnesium aluminosilicate hydrates

The progression of studies in the field of binding materials is moving towards more sustainable and high-performance products; despite this, research applied to the use of restoration mortars in archaeological contexts is still lacking and opened to new findings. The fabrication of these materials requires not only an exhaustive examination of the buildings and their constituents, but also the execution of optimized experimental tests to evaluate their mechanical properties, durability, workability and, above all, compatibility for use in building works with unreinforced masonry, usually found in architectural contexts of cultural interest[1].

Starting with a multi-analytical characterization of heritage building materials and of two different geo-resources used as natural additives and filler in the mixing process, this work aims to enhance understanding of sustainable pozzolanic binders for restoration, developing their cohesive properties through the formation of calcium aluminosilicate hydrates (C-A-S-H) and/or magnesium aluminosilicate hydrates (M–A–S–H).

1.2 From archaeometry to restoration. The use of Euganean breccia and "Ferretto" clay sediments

The additives used to produce new binders were a highly amorphous perlitic breccias from the volcanic outcrops of the Euganean Hills (Veneto region) and clay-rich sediments, defined as "Ferretto" deposits, sampled from different outcrops in the surrounding of Varese (Lombardy region).

The Euganean Hills constituted an important supply basin of stone materials for the city of Padua. Several relevant Roman buildings in the city and its surroundings stand as significant examples of the systematic employment of local geo-resources; recent archaeometric investigations have revealed the presence of Euganean volcanic aggregates including rhyolitic and latitic breccias, used as activators of the pozzolanic reaction. The dominance of highly reactive amorphous silica led to the development of pozzolanic reaction, with relevant structuring of calcium aluminosilicate hydrates which subsequently affected the good mechanical properties of the final structural components[2].

Furthermore, an alternative utilization of peculiar clay deposits ascribed to the Middle Pleistocene and situated in Northern Italy is presented[3]. Multiple recent archaeological and archaeometric studies have demonstrated a relevant use of these materials extracted from the surrounding of Varese in the production of mortars. According to mortars analysis carried out in the excavation site of San Giovanni Evangelista in Castelseprio and in the Torba Monastery, the specific characteristics of the local clay-rich

1 Arizzi, Cultrone 2021, 6-7.
2 Deiana 2018, 114-115.
3 Zuccoli 2000, 62.

sediments influenced the incidence of pozzolanic processes, contributing to the formation of C-A-S-H, AFm phases and M-A-S-H phases[4].

2. Materials and methods

Previous knowledge acquired from archaeological, archaeometric, and geological studies enabled the development of a multi-analytical approach to characterize the geo-resources and standard materials for the production of new binders. A first pretreatment of the materials involved mechanical size reduction and sieving procedures followed by the adoption of particle size analysis (PSA) to obtain a representative granulometric target for both breccia and clay. Microstructural and microchemical analyses were conducted by Scanning Electron Microscopy (SEM-EDS), and a detailed chemical characterization of the materials was performed through X-ray fluorescence analysis (XRF). Furthermore, the mineralogical composition was investigated by means of quantitative phase analysis on X-ray powder diffraction data (XRPD). An intermediate analytical step included thermogravimetric analyses (TGA) performed on both natural additives and oxides used in certain formulations[5]. The multi-analytical approach applied both on the bulk samples of all the employed materials and on the final powders of the two additives, outlined the presence of high silica and alumina contents both in the perlitic breccia (as represented by the high amorphous content observed in XRPD analysis) and in the clay, and a notable rate of magnesium in a group of clays, as shown by XRF analysis and by XRPD in relation to the occurrence of mineralogical phases like vermiculite and clinochlore.

3. First assessment and future activities

In ancient binding systems, the intrinsic heterogeneity of the raw materials, the different condition of the precipitating environment and various mixing practices[6] had a direct influence on the formation of complex composites, frequently leading to the development of pozzolanic processes broadly divided in C-(A)-S-H and M-(A)-S-H phases[7]. The study of historic pozzolanic mortars could represent an initial reference for the experimental development of new materials suitable for restoration and sustainable building practices[8].

Concerning the current study, the subsequent experimental phases focused on the evaluation of detailed strategies of formulation, storage and curing of the binder specimens obtained by mixing natural pozzolanic additives and standard binding materials (oxides and slaked lime). The preliminary mix design criteria were employed on a set of 12 distinct trial formulations, from which 6 potential mixes were subsequently chosen. By setting a standard binder-to-filler ratio of 1:1 (with a differentiation of 1:0.7:03 for the mixes with slaked lime and oxide), their workability has been monitored varying the water content and defining specific mixing procedures. The final samples, subjected to subsequent molding and curing phases, could provide a first insight concerning the definition of possible strategies related to the systematic use for restoration purposes of perlitic breccia and clay soils.

The acquisition of additional data will facilitate the determination of the binder mixes' properties subjected to a curing process ranging from 60 days to two years. Further analysis will clarify the formation of pozzolanic products evaluating their possible suitability for restoration purposes.

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Mechanical and microstructural characteristics of lime-gypsum renders reinforced with hemp fibers

The use of biofibers in construction has been known for centuries. Today we approach their reuse with the awareness that thesethey are sustainable materials in construction that improve thermal and mechanical properties, which also includeincluding the good properties of hemp fibers[1]. TheThis paper presents the development of hemp-based materials will focus on utilizingrenders using novel low-carbon lime-gypsum binders designed by traditional technology. Mixing waste gypsum and quick lime prevents the need for calcining gypsum to obtain air binder (hemihydrate)[2]. This approach reduces the demandneed for natural gypsum and contributes to waste reduction, aligning with circular economy principles and principles of New European Bauhaus which will transform of our societiessociety along the three inseparable values, sustainable of sustainability, aesthetics and inclusion[3].

In this study, the influence of different length of the hemp fibers of different lengths on the mechanical properties of lime-gypsum renders werewas investigated. For this purpose, render mixtures reinforced with different lengths (0.5, 2, 10 and 2010 mm) and different ratios (1, 2 and 5 wt.%) of hemp fibers were prepared. BinderThe binder was prepared withby mixing calcium quicklime (CL 90-Q (R5, P1) and waste titanium waste gypsum in different ratios. (5, 10, 20, 30, 40 and 50 wt. %) with the same consistency. The compressive strength of the lime-gypsum pastes was determined after 7, 28 and 90 days. The phase composition of the binder was determined by X-ray powder diffraction and thermogravimetry differential thermal analysis (TG/DTA). The microstructure of the binder was analysed by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), which indicates the gypsum distribution in the samples.

Figure 1. Dry binder mixture of 80% of quicklime an 20% of gypsum (left) and slaking quicklime and gypsum (right).

1 Rojas et al. 2019.
2 Golež et al. 2018.
3 Coujard et al. 2023.

Binder composed of 20 wt. % of gypsum was selected for further studies. After slaking, mortarsthe renders were prepared by adding ground aggregate grains with CEN standard sand and lime-gypsum putty in a grain compositionmass ratio of 0/1:2 mm.
The workability of renders with added fibers was reduced compared to the reference mixture. The render mixtures were adjusted by adding water to achieve a consistency in the range 190 ± 10 mm. The compressive and flexural strength of the renders was determined after 28 days. The microstructure and binder/fibers interface of the renders were studied using scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). In addition, the microstructure of the hemp-reinforced renders was analysed using micro-computer tomography.
Lime-gypsum plasters are a useful material for the construction of new buildings and the preservation of cultural heritage sites.

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Topic 7

Conservation issues concerning mortars, plasters, renders and grouts. Diagnosis. Decay and damage mechanisms. Case studies

V.A. ANUPAMA, ENRICO SASSONI, MANU SANTHANAM

Salt ingress in consolidated brick masonry systems with lime mortar

1. Introduction

Consolidants are products used in built heritage conservation to improve grain cohesion and adhesion and thereby improve the durability of structures. These fluids of small contact angle penetrate materials, harden within their pores and improve the mechanical strength of the substrates. They aid in reducing the progression of decay and arresting damage[1-2-3]. However, the influence of consolidants on the material durability when exposed to salt weathering demands further research. Salt, dissolved in water, penetrates the material's pores and crystallizes once the water evaporates, inflicting damage. The deterioration due to salt crystallization is due to the hydration pressure, volumetric expansion or crystallization stress. As the extent of damage depends on porosity and pore structure, the change in porosity, pore connectivity and mechanical strength after consolidation is expected to influence the salt weathering resistance and the distribution of salt within the microstructure. The current study focuses on the effectiveness of two consolidants – Diammonium hydrogen phosphate (DAP) and Tetraethoxysilane (TEOS) – on brick masonry systems with lime mortar containing standard sand aggregates during salt weathering. The ingress and distribution of sodium sulphate and sodium chloride ions within the consolidated masonry systems are examined using microanalytical techniques. Hydroxyapatite formation through DAP application on Ca-rich substrate and the development of Si-O-Si bonds, when TEOS is applied to Si-rich substrate, enhances mechanical performance. Their wide use in conservation projects demands further research on their performance when soluble salts are present in the system. A mesoscale investigation into composite systems containing brick and lime mortar facilitates a better understanding of the interaction between masonry components and consolidants.

2. Materials and methods

Fired clay bricks, dry hydrated lime powder, standard sand (Grades I, II, and III), cellulose poultice, Diammonium hydrogen phosphate (DAP), Tetraethoxysilane (TEOS) and distilled water were the raw materials used in the study. The water-to-binder ratio, corresponding to a flow of 165 ± 5 mm, was chosen for the mortars. Discs of 20 mm height and 50 mm diameter were cored out from the brick units. They were immersed in distilled water for about 2 hours before preparing masonry sandwiches. Later, the brick discs with mortar in between were pressed together and kept aside, ensuring the mortar thickness was about 10 mm. The specimens thus prepared were exposed to accelerated carbonation at 3% CO2 (B-DHL-AC-28) or natural carbonation (B-DHL-NC-28). The accelerated salt weathering procedure recommended by the RILEM Technical Committee – TC 271 ASC on Accelerated Salt Crystallization was followed, with a slight modification in the propagation stage to facilitate severe damage. Sodium chloride and sodium sulphate, at 10% and 5% by weight, respectively, were the weathering agents considered for the study,

1 Dal Pozzo et al. 2024.
2 Masi et al. 2023.
3 Sassoni et al. 2016.

which were introduced until capillary saturation of the specimens. After two weathering cycles, the specimens were poulticed and consolidated before the weathering was continued. The mass of the specimens was monitored after each weathering cycle. Backscattered electron imaging (in Apreo-S field emission high-resolution equipment) was conducted on fractured samples (epoxy impregnated and polished) with an intact interface, to examine the salt distribution within the microstructure. Quantitative and qualitative X-ray diffraction (XRD) was carried out for the mineralogical characterization of the samples using MiniFlex Rigaku benchtop PXRD equipment and XPert HighScore Plus v.3 software[1].

3. Results

Consolidated specimens retained more parent material (after weathering and desalination) and resulted in lesser material loss than the unconsolidated specimens after weathering. TEOS consolidation resulted in bimodal differential pore intrusion curve and introduced a critical pore size around 40 nm whereas DAP consolidation retained the critical pore size of 1000 nm. Imaging the brick-mortar interface helped quantify the salt percentage in the specimens. Chloride and sulphate content are significantly lower in the brick phase of the TEOS-consolidated specimens and moderately lower in the mortar phase. The limited ingress of salt into the specimen due to the denser microstructure resulting from TEOS consolidation is confirmed through imaging and point analysis. Salt accumulation on the mortar phase instead of on the brick phase indicates that the breathability of the system is successfully maintained, and the subsequent deterioration will preferentially occur on the mortar phase rather than on the brick phase. The accumulation zone is still within the mortar after DAP consolidation, indicating partial resistance to salt accumulation. Unlike the consolidated specimens, the zone of accumulation is within the brick phase of the control specimen. This response is highly unfavourable as the brick would become vulnerable over prolonged exposure and preferentially deteriorate over the mortar. In general, chloride ion concentration seems higher in the sandwich specimen with naturally carbonated lime mortar than in those with accelerated carbonation. This could be attributed to the higher pore connectivity, permeability and larger pore size of naturally carbonated mortar than accelerated carbonated mortar. Across all the specimens of different consolidation statuses, the interface regions host higher salt concentrations, reinforcing its pivotal role in salt transport.

Chloride infiltration into specimens is more pronounced than sulphates, attributed to the smaller ionic size of the former. In addition to the thenardite phase, gypsum is found in DHL-NC-28 specimens after sulphate weathering. However, gypsum is absent in the accelerated carbonated mortar and brick samples. This could be due to microstructural development, porosity and phase formation during the carbonation process.

4. Conclusions

The study proved that consolidation provided better material retention during sulphate and chloride weathering. Despite the challenge of reduced pore size and connectivity, TEOS-consolidated specimens improved the performance in both individual and composite systems considered in the study.

The breathability of the brick-masonry systems is not hampered through consolidation using TEOS and DAP.

The presence of gypsum was identified after sulphate weathering of naturally carbonated mortar sample due to the presence of portlandite and higher pore connectivity in DHL-NC-28 as opposed **to DHL**-AC-28 specimens. DAP-consolidated specimens showed lesser gypsum because the Ca ions were used mainly for HAP formation during consolidation.

The percentage of chlorides was higher than that of sulphates in the samples collected from the specimens, which could be attributed to the smaller size of chloride ions, higher solubility, and higher mobility compared to sulphates.

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The dark fate of copper-based pigments in fresco painting: preliminary results

1. Introduction and methodology

Copper-based pigments have been used in wall paintings across Europe since Antiquity. The colour and stability of these pigments are influenced by their chemical composition and binding medium. Regarding chemical composition, copper-carbonates and copper-silicates are generally found, the latter said to be more stable. The choice of the binding medium defines the painting technique, in which case we can generally discriminate between a secco techniques, where pigments are typically mixed with an organic binder, or a fresco. In the latter, pigments are dispersed in water and applied onto a fresh lime-based mortar, where calcium hydroxide ($Ca(OH)_2$) plays a crucial role. By its reaction with carbon dioxide (CO_2) it forms calcium carbonate ($CaCO_3$), embedding the pigment particles within the $CaCO_3$ hardened matrix. The initial high alkalinity of this system (pH around 13-14) has been identified as a key factor in their colour alteration, where a blackening process is known to take place due to the formation of blackish copper oxides[1-2].

To deeper investigate the blackening of Cu-pigments in wall paintings, copper-carbonates such as azurite (Cu3(CO3)2(OH)2) and malachite (CuCO3Cu(OH)2), both natural and synthetic, and copper-silicates such as Egyptian blue (CaCuSi4O10, synthetic pigment) and chrysocolla (CuSiO3, natural pigment), where applied both a secco (pigments mixed with egg yolk as binder) and a fresco. The mineralogical characterization by X-Ray Diffraction (XRD) of the raw pigments was carried out before application, and the amount of copper—Cu (in %) present in each pigment was measured by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). After one year at laboratory conditions (18 ±5 °C at 60 ±10% RH), a physical, chemical, mineralogical and micro-textural characterization of the paint mock-ups was carried out by means of stereomicroscopy, Polarised Optical Microscopy (POM), micro-X-Ray Diffraction (μXRD), Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (ATR-FTIR), and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS).

2. Results and discussion

Under naked eye, all Cu-based pigments remained stable when applied a secco (whether they were mixed with egg yolk or with rabbit glue), whereas only Cu-silicates remained unaltered when applied a fresco, particularly Egyptian blue, as chrysocolla showed a slight darkening (Figure 1). In contrast, Cu-carbonate pigments underwent an extensive blackening process (Figure 1).

Regarding the chemical characterization of the raw pigments, the copper content in Cu-carbonate pigments ranged from 25% to 54%, while in silicate pigments, Egyptian blue contained 14% Cu and chrysocolla 36%. As for their mineralogical characterization, other mineral phases were identified depending on their nature (natural or synthetic). For instance, natural azurite and malachite presented impurities related to their natural provenance, such as cuprite-Cu2O or hematite-Fe2O3 in natural malachite, as well as

1 Mattei et al. 2008.
2 Gutscher et al. 1989.

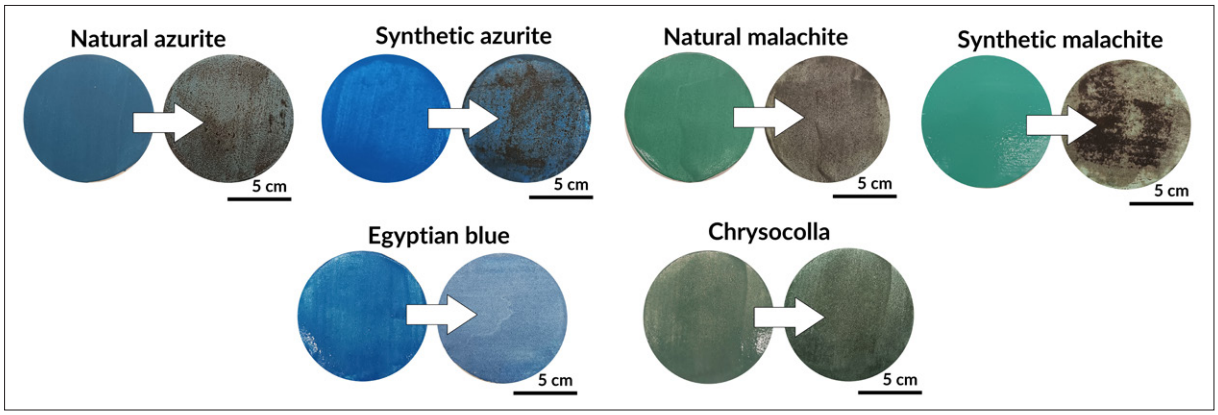

Figure 1. Fresco paint mock-ups after paint application (left) and after 28 days (right) of carbonation of the lime-based mortar.

chrysocolla which had malachite and quartz as impurities, determined by XRD. Synthetic pigments, in turn, presented either calcite-$CaCO_3$ or quartz-Si2O due to the raw materials used in their manufacture. The examination of the fresco paint surfaces using stereomicroscopy revealed that blackening was more homogeneous and widespread in natural pigments such as azurite, malachite and, to a lesser extent, in chrysocolla. Analysis of the paint thin cross-sections through POM indicated that the blackening reached a depth of up to 100 µm in natural-based pigments, and approximately 50 µm in synthetic ones. This was directly related to pigment particle size, as natural-based pigments had larger particles and thus thicker paint layers, whereas synthetic pigments had smaller particles, resulting in thinner paint layers. Unaltered blue and green particles were also observed throughout the paint layer. Surprisingly, copper oxides (such as tenorite, CuO) were identified only in azurite-based frescoes, whilst natural and synthetic malachite and chrysocolla aligned with the previous pigment mineralogical composition, despite undergoing evident blackening. Chemical analyses by ATR-FTIR did not yield conclusive results as the Cu–O characteristic bands were generally obscured by the dominant calcium carbonate signal from the mortar, preventing the detection of pigment related changes. From a micro-textural point of view, areas with higher porosity and heterogeneous texture were observed in all paintings (i.e. natural azurite, Figure 2a), higher in synthetic-based ones (i.e. synthetic azurite, Figure 2b), except for Egyptian blue which showed a homogeneous surface (Figure 2c).
This observation contrasts with traditional fresco wall paintings which typically exhibit a homogeneous and compact calcium-rich layer[3], as has indeed been observed in Egyptian blue, namely the only paint that did not undergo blackening (Figure 1).

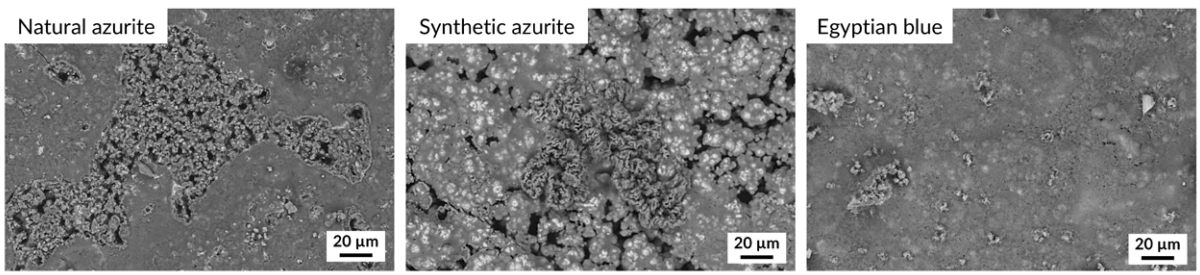

Figure 2. Micrograph by SEM-EDS of the surface of fresco paint samples from natural azurite (left), synthetic azurite (centre) and egyptian blue (right).

3 Piovesan et al. 2012.

3. Conclusions

The extent of colour alteration in Cu-based pigments applied a fresco was highly dependent on pigment origin (synthetic-based paints showed higher micro-textural alterations on the surface) and chemical nature (Cu-silicates pigments were more stable than Cu-carbonates ones). The fact that chrysocolla, which is a Cu-silicate, also underwent slight blackening has to be related mainly to the presence of malachite as an impurity.

The blackening phenomenon observed in our copper-based fresco paint mock-ups was generally attributed to the high alkalinity of calcium hydroxide during the pigment application, which induced the formation of copper oxides, responsible for the colour change of the surface. However, these oxides were not always identified, either because they were in very low amounts (i.e. under the detection limit of the analytical techniques), or because their formation was not the unique reason for this blackening. These preliminary results showed that a deeper investigation on the atomic/molecular transformation undergone by Cu-compounds (especially carbonate ones) under high pH is needed to explain differences in the blackening tendency of pigments. For this purpose, additional studies using X-ray Photoelectron Spectroscopy (XPS) are currently underway. In all, this study sheds light into the fresco wall painting technique and deepens the knowledge on the interaction of copper pigments with the mortar alkaline environment.

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Degraded lime concrete in subaquatic foundation of railway bridge build in 1850 in France

1. Introduction

The maintenance and repair of immerged concrete foundations that support railway bridge piers require a good knowledge of on-site concrete characteristics and its degree of degradation that varies from highly porous structure, micro/macro-fissured structure until decametric cavities development. Indeed, the repairing injected grout based on modern binder as recommended by AFTES[1], needs to be formulated considering the degradation type.

The present communication brings first observations and measurements on a several meters depth lime concrete foundation supporting a railway bridge built in 1850 in South West France. The challenge consists to better understand the possible degradations process in subaquatic environment based on the description at micro and microscale of lime concrete samples after several decades in immerged conditions.

2. Material and methods

The studied structure was implemented using lime concrete considering that modern hydraulic binders were not available before 1900. However, the applied formula or the building method remained unspecified in archives, which imposes to make hypothesis. The tilted or vertical collected cores in Fig. 1 (with 10 cm in diameter) were stocked during one year under air before lab testing, with CO2 contact inducing carbonation. After a 50 cm superficial grey lime concrete (with the presence of mixed surrounding clay-rich soil), a layer of calcareous porous stone was observed overlaying a 3 to 4 meters layer of white lime concrete with 1-2 cm rounded gravels. The cores surface close to the porous stone appeared ochre considering a superficial contamination during the boring. From visual aspect, old concrete couldn't be easily distinguished from a modern one, except by its light colour. The apparent "intact" pieces of concrete core were separated by large empty volumes filled by remaining gravels covered by lime binder. No porous areas were observed by eye which suggested that degradation occurred as in a calcareous natural karstic area with the development of large cavities controlled by surface dissolution induced by the river water passing through the concrete structure. To investigate the material variability, samples were collected in various locations for mineralogical analyses using XRD (using a D8 advance diffractometer from Bruker coupled to Rietveld quantitative estimation with TOPAS software) and to scanning electron microscopy (using an environmental SEM Quanta 400 from FEI) completed by mercury intrusion porosimetry (using an Autopore IV from micromeritics).

3. Results of characterization and discussion

XRD measurement on lime mortar revealed the presence of 34 to 49% of quartz (from siliceous sand) associated to feldspars (albite and microcline less than 10%), 25 to 32 % of CaCO3 (with small trace of vaterite in white inclusion of unreacted lime with remaining C2S, C4AF, gypsum). No portlandite was

1 AFTES 2006

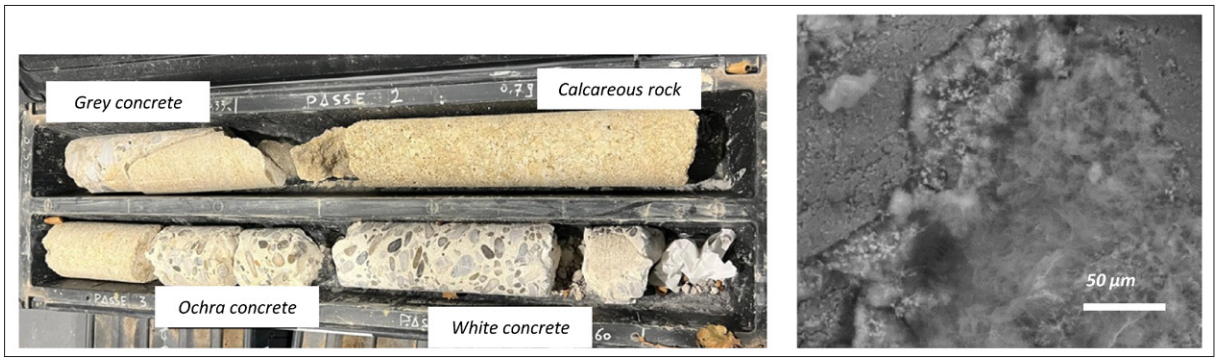

Figure 1. (left) Lime concrete core from railway bridge foundation manufactured in 1850. (right) SEM image of lime mortar showing cementitious hydrates under gel/sheet/filament forms and carbonates (small white points) intimately mixed and homogeneously spread in matrix whatever the collected samples positions in the core.

detected whatever the depth of collect, while a few percentage of muscovite/illite clay coming from neighbouring soil was observed. Amorphous phase estimated by Rietveld method applied on the ground material mixed with 10% corundum, represented 11 to 31% of the mortar. The presence of cementitious hydrates (CASH, CSH) was confirmed by SEM observation with the presence of micrometric typical phases under sheet/gel form. The pore size measurement indicated mainly one pore families around 100 nm with the presence locally of micropores around 1 µm associated to a possible dissolution initiation of the material. The Ca2+ leaching by percolated site water in the porous lime mortar evolving over time was not visible at such scale. Compressive strengths measured on samples varied between 3.7 and 6.9 MPa, while the density was around 2.06-2.23 g/cm3 and the permeability reached 1,3.10-9 to 9,2.10-12 m/s. Considering the mineralogical composition and the microstructure, questions arose from the lime type used for the concrete manufacture in 1850 and the origin of carbonates. Hydraulic lime (NHL) or quick lime with pozzolan addition may have be used on site, which agreed with the remaining aluminum content in mortar around 1.7-3.9 g/kg. Slow pozzolanic reaction in presence of alumino-silicates (added pouzzolan or burnt clay-rich Ca-carbonated rock) agreed with the portlandite disappearance. On long term, all portlandite was consumed by dissolution, releasing OH and inducing alkaline medium. A phenolphthalein test showed that alkalinity didn't totally disappear after several decades in subaquatic environment. The released Ca2+ may then combine with Al or Si from pozzolan, burnt clay of cementitious anhydrous phases, to form hydrated cementitious products. A quantitative mineralogical calculation should help to identify the lime formula in next step.

Parallel to hydration progress, carbonation occurred simultaneously conducting to the nucleation of CaCO3 intimately mixed with cementitious hydrates. If carbonates doesn't come from aggregates in mixture or contamination by site material, the 25% carbonates were formed at one moment until lab tests: during the lime concrete manufacture, during the material life on site with potential drought period conducting to the concrete desaturation (in absence of river water), during its life under water imposing a saturated state, during its extraction from site with drilling fluid used to bore, or during the transport and storage under air during one year before the lab tests. Biological alteration with biocimentation may act too under water, as well as the water composition in term of CO32- concentration. However, the carbonation process is known to be a slow process under air with progression of few mm or centimetre from the material surface, while immerged conditions prevent the gas penetration in cemented structures. However, the high amount of micropores in lime concrete may contribute to accelerate the carbonation process. Furthermore, the large cavities corresponding to the empty areas between cores pieces might conduct water until the center of the foundation, favouring global carbonation until its heart explaining advanced carbonation rate until several meters depth. The lime purity and quality used for implementation could also contribute to the carbonates presence with local lime kiln producing bad quality lime with

uncontrolled temperature used as supplier. Remaining un-calcined clay/carbonated in lime may explain that calcite appeared whatever the depth of sample collect. A dating method to investigate the CaCO3 age or some cathodo-luminescence could bring information to discriminate several origins of carbonates. Finally, the process of implementation needs to be also questioned: as lime mortar was manufactured on site by bringing industrially or locally manufactured lime, the 4m-thickness foundation massive was implemented layer by layer from poured and self-compacting mortar. A better knowledge on the applied procedure in past century and site history should help to confirm the process. Furthermore, the implementation potentially layer by layer required the hardening of underneath layer before the pouring of the next one, which imposed a several months duration of work. So during such time, a superficial carbonation of air-exposed layers might occur following a slow process. However, no interface between layers was observed but as a coincidence, the cavities formed by dissolution appeared repeatedly on cores suggesting a potential role of interfaces as contact defaults in the development of preferential ways of water penetration and dissolution process initiation.

4. Conclusions and perspectives

Finally, the microscale characteristics of a lime concrete in buried foundation manufactured in 1850 was described as well as its degradation and by dissolution forming cavities. Parallel to the possible role of carbonation remains an open question.absence of remaining portlandite, carbonates were observed whatever the depth of sampling and several origins were discussed as well as the nature of used lime. Further analysis, usinganalyses based on methodologies developed for ancient mortars in bricked building should bring complementary information as well as the RILEM TC CUC (launched in 2025) dealing with the carbonation in modern concrete under air but also in buried/immerged conditions especially for the(-petrography, quantitative mineralogical calculation of Life Circle Analysis (CO2 adsorption) of recycled concrete aggregates from demolition waste. To prepare the future, the past needs to be studied. ...) are required to complete this preliminary study.

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Water absorption in multilayered medieval wall painting plaster introduced during hydrogel treatment

1. Introduction

This study examines the penetration of retained water originating from hydrogels into medieval wall painting plaster (replicas and original material). The aim is to investigate how plaster composition and type of gel influence water penetration, thereby providing a basis for predicting and understanding the effect of gel treatments on lime-based wall paintings. Hydrogels are widely used in conservation treatments to ensure that penetration of moisture and cleaning agents is limited to the surface or near-surface of the treated material. In recent years, hydrogels have also shown promising results in cleaning and desalination of Danish medieval wall painting plasters, the advantages being e.g. the enabling of treating water-sensitive areas and reducing the redistribution of surface ions to deeper parts of the material.

The hydro-physical mechanisms of hydrogels are fundamentally different to those of porous building materials. Porous materials absorb water due to capillary action determined by the materials' pore number and sizes. Hydrogels are constructed as three-dimensional networks of hydrophilic polymer molecules interconnected by chemical or physical bonds. The gel network absorbs and holds water due to the same mechanisms as linear polymers mix with water in a solution, and is, thus, balanced between the polymers' solubility in water and the elasticity of the polymer network. When water-filled hydrogels are attached to dry porous materials, the water retention/absorption of the two materials is opposing, and water transfers from the gel to the pore network at a speed determined by the properties of the two materials. The retained water absorption from gels to porous building stones has previously been studied[1]. However, Danish medieval wall paintings constitute a more complex multi-layered composition, as the paintings are executed on thick layers of limewash applied to a single layer of very lime-rich pure air-lime plaster. In a previous study on Danish medieval lime plaster, the capillary water absorption from a "free" water reservoir (following the standard EN15801) was shown to be dependent on the binder-to aggregate ratio of the plaster, as increased binder contents enhanced the water absorption rates[2]. In addition, it was shown that in multilayered wall painting plaster, the water absorption proceeded in phases. The first phase was affected by the structure of the limewash, then by the structure of the plaster surface, and finally by the structure of the plaster bulk. This present study examined whether the retained water absorption from gels (made from agar and poly(vinyl alcohol) follows the same patterns, and to what extent the gels reduce the absorption rate. Due to the water retention induced by the gel, an increased impact from the plaster's near-surface structure (the initial phases shown by EN 15801) was expected.

2. Materials and methods

Measurements were conducted on medieval wall painting plaster in Lillerød Church (from the Gothic period, dated 1470-1480 AD) and on replica specimens comprising plasters with three different binder-to aggregate ratios, with and without application of limewash. All replica plasters had binder contents in the

1 Sansonetti et al. 2023.
2 Bartholdy et al. 2025.

range found in Danish medieval wall painting plasters; one being binder-poor (B:A 1:1) in comparison to an average medieval plaster, one with a similar binder content as the plaster in Lillerød Church (B:A 1.4:1) and one being binder-rich (B:A 3:1) in comparison. Binder contents were determined by point counting thin sections of plaster samples. As the mortar mixing method has been shown to be fundamental in achieving the very high binder contents found in the medieval plasters, the test mortars were made using the (wet) hot-mixing technique, characterized by the addition of sand at the same time as the quicklime undergoes the slaking process. For the mortars, powdered quicklime (CaO) with the chemical and reactivity specification CL90-Q (R5) and siliceous sand with grain sizes mainly below 1 mm were used. The mortars were applied to cylindrical brick specimens (D: 50 mm, h: 50 mm, prod. Falkenløwe) in a 7 mm thick layer and left for carbonation for 1 year and 8 months at 70% (±5) RH, 20˚C. Three layers of limewash (total thickness 0.3 mm) prepared from well matured (> 70 years) lime putty from Roskilde Cathedral lime pit were applied to half of the replica specimens (labeled LW). Laboratory measurements were conducted on plasters detached from the brick. Further details on the test plasters are available in Bartholdy et al.
The water absorption was tested by applying two different gels, each representing different gel types commonly used in conservation. Agar gels (AA3) were prepared from the commercially available product Agar Art by mixing 3% (w:w) agar powder in MilliQ water, heating to boiling point and casting in a thickness of approx. 3 mm. Poly(vinyl alcohol) gels (PVA) were the readymade product Nanorestore Gel® Peggy 6 with a thickness of approx. 1 mm.
Water emission/absorption from gels was tested by attaching circular sheets of gels (D: 27 mm) to the plaster/limewash surface and repeatedly detaching, weighing and re-attaching the gels. Throughout the tests gels were covered with parafilm to minimize evaporation. The water emission/absorption rate (WAR) was found as the slope of the trendline when plotting the amount of water emitted per unit area, Q (kg/m2) as a function of the square root of time (t1/2). Due to the previously described absorption phases, the slope was reported for both the initial phase, measured during the first minute (WAR1) and for the later, stabilized phase (WAR2). Water absorption from gels was compared to the water absorption from a “free” water reservoir obtained by the standard EN15801.

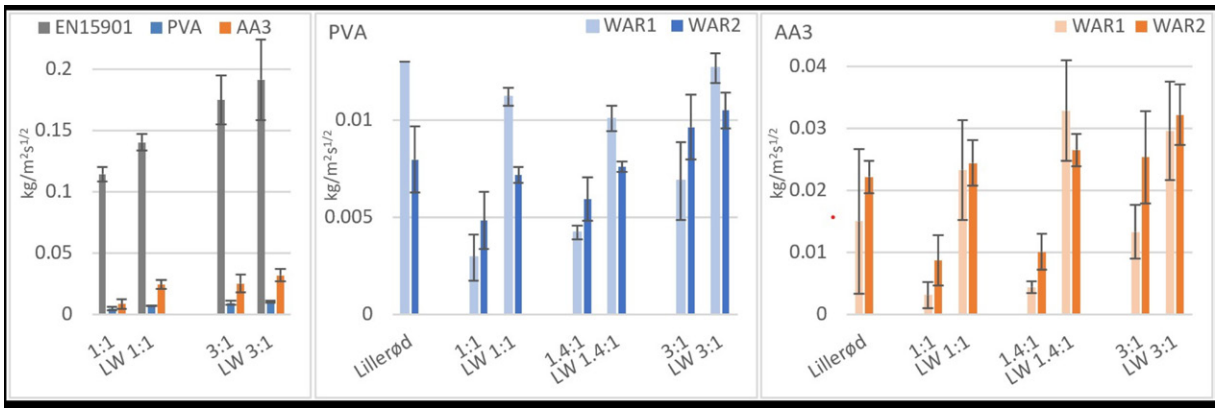

Figure 1. Left: water absorption rate (WAR2) obtained following EN15801 compared to those obtained from gels. Center and right: water absorption rate (WAR1 and WAR2) from hydrogels made from poly(vinyl alcohol) (PVA) and agar (AA3). _:1 refers to binder-to-aggregate ratio (B:A) in replica plaster and LW designates specimens with limewash.

3. Results and conclusions

The experiments showed that water absorption was clearly restrained when originating from gels compared to the water absorption obtained from a “free” water reservoir (EN15901) (Figure 1). For PVA gels, the water absorption rate was reduced by up to 96% compared to that obtained by EN15801, whereas the agar gels reduced the absorption rate up to 92%. The previously described phases of water absorption found by EN15801 were also mirrored by absorption from gels. Hence, in the specimens without

limewash, a reduced water absorption in the initial phase (WAR1), followed by an increased absorption rate (WAR2), was shown. It was previously suggested that this phenomenon was caused by dense zone in the plaster surface2. Similar to the "free" absorption (EN15801), the later phase was clearly affected by the binder-to-aggregate ratio in the plaster, as the plaster with the highest binder content (3:1) showed the fastest absorption, whereas the binder-poorest plaster (1:1) induced the slowest. In the limewashed specimens (LW), a significantly increased initial absorption (WAR1) was shown. The later absorption rate (WAR2) was also significantly increased compared to those measured in the non-limewashed specimens. This either shows that with the restrained water absorption from gels, most of the water only penetrates as deep as the limewash layer (0.3 mm), or that the limewash application induces enhanced water transport from gel to plaster. Further investigation of the water penetration depth will shed light on this issue. The results obtained in medieval wall painting plaster in situ (Lillerød) gave comparable results to those measured in limewashed replica specimens with the same binder-to-aggregate ratio (LW 1.4:1). However, no difference relative to the somewhat binder-poorer (LW 1:1) plaster was revealed. In contrast, the binder richer (LW 3:1) plaster showed significantly faster absorption.
These practical experiments, thus, show that water absorption during hydrogel treatment of multilayered medieval wall painting plaster depends not only on the water-retaining forces of the gel, but also significantly on the capillarity of the treated substrate. Especially the capillarity of the outer surface layer affects the water absorption rate. The findings enable a better prediction of water uptake during gel treatment of lime-based wall paintings.

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Frescos restoration of the Lazzaretto Chapel in Ossona

1. Historical overview

The Lazzaretto Chapel was built in the 17th century, during one of the heavy plagues that struck Ossona (MI) and the province of Milan, late 16th/early 17th century. It became private property and was then donated by the Bienati family to the municipality of Ossona in 2003. The building required restoration work on its fresco-decorated walls, and some surprises were revealed during the latest restoration project, which will be presented here.

2. Location and description

The building stands on a flatland along the road to Casorezzo(MI), next to the Villoresi canal. It has simple architectural lines[1-2]. The exterior is rendered without decoration. it is a single nave volume with a gabled wood roof. The façade is characterised by two small symmetrical circular openings on either side of the front door placed in the middle. The exterior is rendered without decoration. Inside, the nave shows a wooden ceiling, and the walls are all covered with frescoes.

3. State of conservation of the chapel before the latest restoration

The first restoration was carried out in 2004 with contributions from private citizens and local businesses and mainly focused on the pictorial apparatus and rising damp issues. But the building observed in 2016, 12 years after, presented again: 1) Loss of the pictorial film, mainly on the north wall where the altar is; 2) Moisture infiltration from the roof reaching the floor and running vertically through the walls and in addition 3) Vertical cracks causing stability problems, especially in the frescoes on longitudinal walls 4) Vertical crack on the keystone of the main entrance archway; 5). Presence of cementitious mortar basement running the entire outer perimeter of the structure; 6) The inner perimeter, up to a height of 110 cm, showed a lime mortar render (carried out in 2004) with large quantities of acrylic resin (Primal® AC 33) in the composition. This resulted in a glossy film that did not allow the putty lime paint, to adhere to the substrate, causing loss of colour. The frescoes in 2004 were dry cleaned, the lacunae restored with lime mortar and repainted with rigatino technique.

In 2017, significant tile slippage occurred in several places on the roof, creating gaps that allowed rain to enter first the attic and later the chapel. On the south facade, the central crack above the main entrance and the cracks on the longitudinal walls were still clearly visible but not worsened. On the contrary, the walls showed a progression in degradation with severe deterioration due to moisture and consequently loss of colour and salt efflorescence. The north wall has suffered a greater decay of the frescoes, with loss of the original pictorial film as well as of the texture and colour of the retouches made during the 2004 restoration. The decay of the lime pictorial film in the lower part was also advanced.

1 Cultural Heritage Catalog of Lombardy (last access on 13.3.2025).
2 Archives of Ecomuseo di Parabiago (last access on 13.3.2025).

4. The latest restoration intervention

Given the progressive deterioration of the frescoes, a new restoration was planned in 2019. First chemical and microscopic analyses were carried out on several samples of mortar and paint film[3].
After a general visual assessment and once the results of the chemical analysis had been evaluated, the mortar that had been used in the 2004 restoration was removed and the following works were carried out[4][5]: a) demolition of non-congruent mortars; b) repairing of the mortars with putty lime, river sand and coloured earth; c) filling of the smallest lacunae with sieved sand, putty lime and coloured earth; d) dry cleaning with wishab sponge; e) pictorial retouching where needed: lime on new mortars with chromatically suitable earths incorporated into the compound and with Winsor & Newton watercolors in undertone glaze, on minor abrasions.

4.1 Discoveries made during restoration

The removal of the plaster of the previous restoration showed first unexpected different masonry textures: in the northern wall (the apse), a different type of masonry has been found without being interlocked with perpendicular walls. It is made entirely of brick and lime mortar, unlike the others, which are made of bricks mixed with river pebbles. The building therefore may have been shortened over centuries. In addition, the removal of the plasters revealed massive chemical cut on three of the four perimeter walls of the chapel. On the east wall, along the street, injections were performed on two levels (at ground level and 30 cm high) and a situation of total dryness of the walls was observed. Two openings appeared, closed in a second times and hidden by the plaster, now forming vertical and horizontal cracks of discontinuity. The openings were closed with large river pebbles and clay soil masonry (Figure 1).

5. Discussion and Conclusions

The execution of the intervention was challenging, as it was difficult to get the new mortar to adhere, which extended the working time. Several layers of lime render were applied: float coat + finish coat + pigmented finish coat, with continuous wetting of the surfaces. A total dusting of the surface with soft brushes and a vacuum cleaner was then performed. Wishab was used on the side walls and demineralized water and soft sponges on the central wall. After being pigmented with natural earths (according to colour samples), no lime retouching was necessary on the new mortars of the side walls. Under the central fresco, the original lime colouring was applied, with the architectural construction of an altar, respecting the traces left after the demolition and erasing of the motif proposed in the 2004 restoration. At present, 6 years after the intervention, no signs of mutation can be seen on the wall surfaces or in the entire pictorial layer, whether original or non-original.
An observation related to the presence of chemical cut is intended to be reported here. The chemical cut has dried the masonry correctly, but has caused a differentiated deterioration of its mortar joints over time: this is particularly noticeable where there are lime mortar joints, but is not observed where the masonry of the infill of the openings is made with clay earth mortar (Figure 1), typical of the area and widely used in construction from the 1000s to 1600s. One explanation may lie in the different nature of the two components: the lime-only one is stiffer and more brittle, and therefore more prone to exfoliation upon drying, than the earth-based one, which is less brittle and retains moisture longer. Although the chemical cut method was effective in removing rising damp, it proved unsuitable for preserving the frescoes in this chapel.

3 Soroldoni 2019.
4 Frezzato 2009.
5 Matteini and Moles 2007.

Figure 1. The Lazaretto Chapel in 2019, after the removal of the mortar from the 2004 restoration.

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Effect of type of plasters in detection of anomalies on masonry panels by IRT and GPR investigations

1. Introduction

Non destructive testing (NDT) is fundamental in the knowledge process of architectural heritage buildings, especially in the diagnosis phase and in evaluating the effectiveness of interventions[1].

Among ND procedures, infrared thermography (IRT) and ground penetration radar (GPR) are usually applied onsite to the surface of masonry elements (e.g., walls, pillars and vaults). They aim at identifying possible anomalies related to inclusions or deterioration due to the presence different materials and/or onsite conditions[2-3].

An experimental campaign was carried out to compare the results of IRT and GPR applied to the most common masonry types of historical buildings (regular brickwork, irregular stonework, and a mixed one) covered by different types of plasters (traditional fresco of natural hydraulic lime - NHL, and hydraulic lime-based – HL, or cement-based - C ones). Some of the modern plasters refer to an intervention technique, i.e., jacketing, which is commonly applied to masonry walls to improve their mechanical performances, especially in seismic zone. In such case, plasters were reinforced by welded steel meshes or innovative BTRM (basalt textile reinforcing matrix, including thin steel threads). Artificial anomalies were realized at various depths from the surface, simulating detachments at the plaster-masonry interface or inclusions of other materials at the masonry face level. Three three-leaf walls with dimensions of about 120x115 cm2 in facades and 38-45 cm thick were built, and the effect of interventions were investigated by NDT on their main faces (Table 1).

Mockup	Plaster type/ thickness	Reinforcement/thickness	Anomalies at plaster-masonry interface	Anomalies at masonry surface
Mixed masonry	NHL / 20 mm *(fresco)*	none	Teflon sheets (dim. 2-12 mm)	Removed stone and partial bed joints; inclusion of wooden beam (160x130 mm^2) and steel plate (150x100 mm^2) with steel anchoring tie (12 mm)
	HL / 20 mm	BTRM mesh+thin steel threads / 1 mm	-	Inclusion of steel bar (12 mm)
Brickwork	C / 20 mm	none	Teflon sheets (dim. 1-12 mm)	Removal of bricks and partial bed joints; inclusion of wooden joist along a brick course and a steel bar (10 mm)
	C / 50 mm	Welded steel mesh / 6 mm	Teflon sheets (dim. 2-12 mm)	Removal of bricks and partial bed joints; inclusion of steel nails
Stonework	HL / 20 mm	none	Teflon sheets (dim. 2-12 mm)	Removed stone and partial bed joints; inclusion of wooden joists (50x50 mm^2)
	HL / 30 mm	BTRM mesh+thin steel threads / 1 mm	Teflon sheets (dim. 1-12 mm)	Removed stone and partial bed joint; inclusion of steel nails

Table 1. Description of mockups and related anomalies in their main faces.

1 Binda et al. 2000.
2 Grinzato el al. 2002.
3 Harry 2009.

2. Experimental analysis

2.1 IRT acquisitions

The IRT investigations were carried out on the mockups in passive mode (solar irradiation) with a Flir T620 thermocamera placed 2 m from them.

Larger Teflon sheets (about 10x10 mm2), as well as the metal anchoring tie and the wooden beam were well identifiable in the mixed masonry panel covered by fresco (Figure 1.a). As for the other mockups, sub-surface anomalies were better recognizable in the stone masonry panel (HL-based plaster) than the brick one, where only metallic elements in the case of the thinner covering were mostly detected (Figure 1.b,c).

2.2 GPR acquisitions

The GPR investigations were applied to the mockups in monostatic mode (one side only) along vertical arrays 10 cm spaced, by using an IDS 2GHz antenna.

Results showed a better detection of the anomalies in the brick masonry panel (C-based plaster) than the stone one, particularly for the metal inclusions. Loss of material simulated by holes were also visible, as well as the largest Teflon elements, in all the mockups (Figure 1.d,e,f). Small Teflon elements and wooden inclusions were not detected.

Furthermore, in the cases of the brick and mixed masonry mockups, the steel meshes included into the jacketing intervention (either as welded rods or thin threads integrated into the BTRM, respectively) were well identified; however, they shielded the possible anomalies behind them.

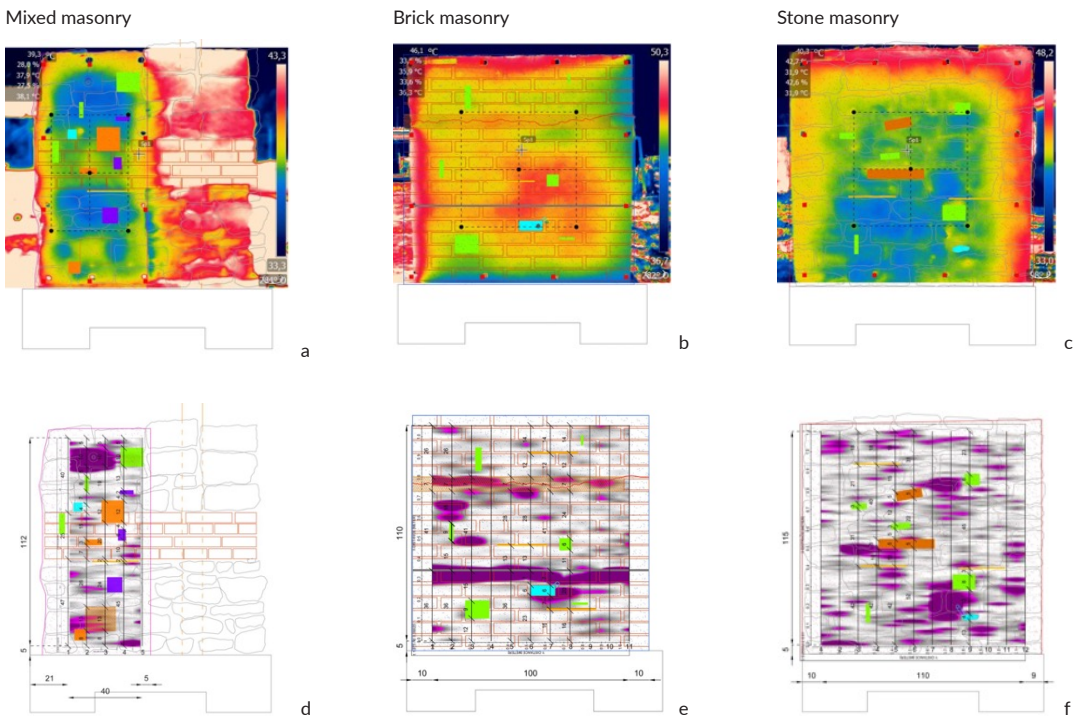

Figure 1. Example of comparison of IRT (a,b,c) and GPR (d,e,f) results on the three mockups.

3. Conclusions

This study contributed to clarify that:

- IR thermography and GPR investigations can be complementary to a broader assessment of the conditions of plasters covering historical masonry. This concerns not only the inspection depth, but also the type of anomalies (e.g., type of materials) that can be found in a wall.

Results showed, that GPR could inspect subsurface anomalies from 3-4 cm to 20-30 cm, thus including the state of part of the substrate; IRT can inspect up to 5-6 cm from the surface, which mainly encompasses the plaster-masonry interface.
IRT was not able to detect the steel nets (neither the welded rods nor the thin threads in BTRM), but only the small metallic elements (i.e., nails, rods) in case of thin plasters, which were all instead well identifiable by GPR. The portions of wooden joists emerging from the masonry façade were identified by IRT and not by GPR.
- Both methods permitted to identify the texture of the various types of walls covered by the plasters; however, the presence of regular steel meshes hides subsurface changes in material and/or possible defects, particularly in GPR investigations.
- The types of plaster influenced the results in different ways. As regards GPR acquisitions, subsurface anomalies were better identifiable in the case of cement-based plastered panels, rather than lime-based one, although the higher thickness of the cement cover. This was probably due to the interaction of the regular vs irregular texture of brick and stone masonry, respectively. Conversely, IRT acquisitions emphasized the presence of anomalies in the lime-based plastered panels. This is because IRT results are influenced by the thickness of the plaster but also by its nature: indeed, cement-based plaster absorbs and emits less heat than lime-based plasters, thus shielding the subsurface elements.

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The degradation mechanisms in historic tiles in Brazil

1. Degradation mechanisms of historic tiles

The degradation of ceramic coatings in historic buildings is a complex process, influenced by multiple factors that can act either separately or in combination, accelerating the deterioration of wall coverings. In this context, this work intends to analyze the main degradation mechanisms that impact historic tiles applied in the colonial period in Brazil. In buildings prior to the 19th century, Portuguese-origin tile panels and plastered coatings were common, especially in the early periods of the colonization. The mortars used in these old constructions were made from local materials, such as clay, sand, lime, and in some cases, organic substances like blood, animal manure, and whale oil, although the latter is no longer considered in more recent studies[1].

Until the 18th century, coatings in Brazilian buildings were scarcely altered, predominantly using clay, lime, and sand, with whitewashing made from lime derived from seashells, which was widely used along the Brazilian coast. Later, lime and cement derived from limestones and dolomites were introduced, replacing the shell-derived lime. That way, some historic buildings were made with more porous materials that allowed functions such as thermal protection, water barrier, and air circulation, with moisture being rapidly evaporated by lime mortars.

In this context, it is relevant to state that old mortars play a crucial role in the conservation of buildings, functioning as an "articulated membrane" that absorbs stress and moisture, helping preserve the structure and playing an important role in cooling the building. The cycles of wetting and drying also favor the recrystallization of calcium carbonate in microcracks, which contributes to the durability of the materials[2]. However, when impermeable coatings, such as tiles, are applied, the moisture evaporation process can be hindered, aggravating moisture problems and causing cracks or detachment of ceramic pieces[3].

Therefore, the porosity of historic masonry and mortars is an important factor to consider in the conservation of coatings. It influences the hygroscopic behavior, degradation mechanisms, and material durability, controlling the retention and evaporation of moisture, air penetration, and carbonation of calcium hydroxide. The bond between the tiles and the substrate is another relevant factor in the degradation processes, being influenced by some factors, such as: the composition of the mortars, the amount of air, water retention, fluidity, the material's aging conditions, and exposure to different climatic conditions[4].

In addition to this, the study of the causes of degradation of historic tiles also reveals that physical damage is caused by factors such as external aggressions (sunlight incidence, rain, wetting cycles) and the fragility of the tiles themselves. Moisture retained in the walls, especially when coated with impermeable materials like tiles, can cause infiltration, stains and detachment of the pieces. Besides, moisture expansion (EPU) can also compromise the adhesion of ceramic pieces, leading to cracks and fissures in the coating.

It is also important to discuss that the presence of dirt, infiltration stains, cracks, and losses are also

1 Comerlato 2010.
2 Santos e Veiga 2012.
3 Carasek et al. 2014.
4 Botas et al. 2020.

common problems, more intense on facades exposed to adverse climatic conditions. The degradation of ceramic tiles in historic buildings is usually more pronounced in facades exposed to harsh environmental conditions, such as rain cycles, pollution, and thermal expansion due to sunlight, compared to tiles in indoor settings that are generally shielded from these factors.

These highlights are reinforced by some research conducted in cities such as Lisbon[5] and southern Brazil[6] have shown that ceramic coating degradation is largely caused by moisture from heavy rainfall, capillary rise, or damaged plumbing. The thinner supporting walls in Brazilian buildings favor faster moisture evaporation, contributing to the conservation of the tiles.

Another important factor to consider is the action of salinity, particularly the ability of certain salts to absorb moisture (hygroscopicity) and dissolve through air humidity, then recrystallize when ambient moisture decreases. This process can cause continuous damage, even without water transport through the masonry, as salts cycle through dissolution and recrystallization. Additionally, water circulation in masonry can make construction materials and soils potential sources of soluble salts, which are often difficult to detect due to their inaccessibility. The porosity, chemical characteristics, and condition of materials further influence tile resistance to salt effects[7].

Thus the degradation mechanisms of tiles include physical, chemical, and biological agents. Physical agents involve damage caused by mechanical shocks, moisture, temperature fluctuations, and production defects. Chemical agents refer to attacks by salts, acids, or alkaline solutions that affect the ceramic body and the glaze. Biological agents include the growth of fungi, algae, and bacteria in humid environments.

Therefore, the conservation of historic tiles depends on a detailed analysis of the degradation mechanisms, considering factors such as exposure to external agents, moisture in the walls, and the quality of the materials used. Accurate damage diagnosis requires consideration of these multiple factors, making preventive maintenance essential and fostering an understanding of the interactions between building materials, environmental conditions, and degradation processes.This knowledge can lead to better and more effective maintenance solutions to ensure long-term preservation, as illustrated by the representative set of the most common damages identified in Brazil's Northeast region, and their corresponding degradation machanisms listed in Table 1.

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5 LNEC, 2011.
6 Curval et al. 2012.
7 Brito 2017.

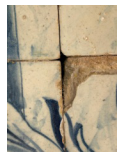
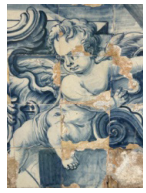
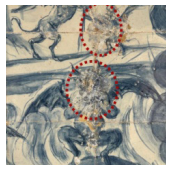
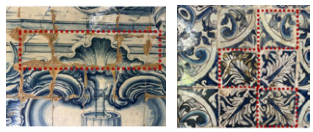
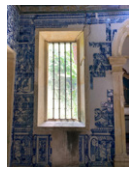
Damage	Picture	Mechanism of degradation
Fragment loss/ detachment		Physical (shocks, moisture or environmental conditions: rain, pollution, sunlight, ...)
Fissures/cracks		
Craquelure/gretamento		Physical (Thermal fluctuations and moisture expansion)
Eflorecence		Chemical (Action of salinity)
Concretion		Chemical (Deposition of insoluble materials like calcium or magnesium salts over the surface)
Discoloration/stains		Chemical (Moisture, material incompatibility or atacks of acid or alkaline solutions)
Loss of glaze		Physical and chemical (Moisture, salt crystallization or environmental conditions)
Powdering/disaggregation		Physical and Chemical (Salinity, porosity, or humidity cycles)
Biological colonization		Biological (xylophagous organisms, fungi, algae, insects...)

Table 1. Summary of the most common damages observed in historic tiles in Brazil and their respective degradation mechanisms

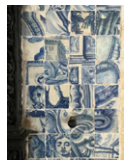
Damage	Picture	Mechanism of degradation
Inadequate interventions/ disorder		Human action (Inappropriate cleaning, use of unsuitable materials, vandalism, graffiti, surface residues)
Foreign elements		

Table 1. Summary of the most common damages observed in historic tiles in Brazil and their respective degradation mechanisms (continued).

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A State-of-the-art Review on the Vulnerability of Historic Lime Mortars in Urban Environments

1. Introduction

The permanence of lime mortars on historic urban surfaces has been increasingly threatened by atmospheric pollutants. Traditionally valued for their physicochemical compatibility with historic substrates, these materials now face challenges arising from acid gases, suspended particles, soluble salts, and intensified cycles of humidity and solar radiation. Based on an integrated analysis of recent studies developed over the last two decades, this work reinforces the urgency of understanding the degradation mechanisms triggered by these agents and of identifying mitigation strategies aligned with preventive conservation principles.

2. Carbonation and its effects

The carbonation process, although traditionally associated with the hardening and consolidation of aerial lime mortars, is also affected in contaminated environments. Recent literature indicates that the presence of alkalis in the mix, combined with CO_2 uptake and moisture, can result in the formation of deleterious alkaline salts that crystallize within the pores. In porous structures, such crystallization can lead to microcracking and loss of structural integrity. Moreover, incomplete carbonation—common in environments with high humidity and low ventilation—leaves the binder more vulnerable to secondary chemical reactions and aggressive environmental agents[1].

3. Impacts of polluted atmosphere on microstructure

Urban environments rich in sulfur dioxide (SO_2) promote sulfation in lime-based mortars, resulting in the formation of gypsum and, in hydraulic systems, syngenite. These products accumulate on surface layers and, in the presence of moisture, cause binder leaching and microcracking due to shrinkage. Experimental studies report reductions in compressive and flexural strength, with aerial mortars showing greater vulnerability[2-3].

Artificial aging tests also reveal the formation of calcium sulfite hemihydrate as a dominant product of the reaction between SO_2 and lime compounds. The geometry of the resulting crystals varies according to the presence of additives: elongated needles, plates, or spheres form depending on the modification of the internal surface of the matrix, directly affecting its cohesion. Upon exposure to rain, these crystals dissolve, further aggravating surface instability[4].

Although these products form superficially, their recurrence is sufficient to compromise exposed coatings, leading to detachment due to loss of cohesion, reduced density, and increased porosity. In mortars

1 Rodriguez-Navarro et al. 2023.
2 Lanas, Sirera, Álvarez 2005.
3 Lanas, Sirera, Álvarez 2006.
4 Izaguirre, Lanas, Álvarez 2010.

containing potassium and sodium — such as those with volcanic ash or impure binders — expansive secondary salts may recrystallize within the pores, further promoting internal stress and deterioration[1].

4. Preventive strategies and future directions

In response to the vulnerability of lime mortars in polluted urban contexts, recent research emphasizes two guiding principles for mitigation: preserving the original material properties and reducing susceptibility to pollutants. Among promising approaches are treatments with hydroxide and silica nanoparticles applied by nebulization. These enhance surface cohesion and reduce porosity while maintaining compatibility with mineral substrates[5]. Photocatalytic coatings are also being explored, as they promote the degradation of NO_x and SO_2 when exposed to light. These transparent films provide a self-cleaning effect without compromising vapor permeability or aesthetics[6].

Advancements in characterization tools have improved the diagnosis of areas affected by pollution. Techniques such as X-ray fluorescence and mass spectrometry help identify compounds formed on the surface of mortars, while hygrothermal simulations assist in predicting material behavior in response to climatic variations and continuous exposure to pollutants. Efforts are also underway to incorporate artificial intelligence in the analysis of environmental and pathological data, to enable more accurate interventions and early detection of degradation processes.

In parallel, the study of historical construction practices has also revealed valuable approaches to material durability and environmental performance. Roman construction systems — notably those based on pozzolans and hydraulic binders with amorphous phases — demonstrate high performance in humid and aggressive environments. These materials, in addition to being highly durable and compatible with historical buildings, hold potential to inspire contemporary low-impact binders, in contrast to Portland cement, whose production emits around 0.87 kg of CO_2 per kilogram of clinker[7].

The conservation field is increasingly moving toward a more integrated and predictive approach that combines traditional knowledge, scientific advancements, and a commitment to sustainability. Beyond the goal of preserving the longevity of historic lime mortars, this movement aims to translate the technical expertise embedded in centuries-old materials and techniques into solutions applicable to contemporary construction. By adapting preservation strategies to different climatic and urban contexts, not only is the effectiveness of interventions enhanced, but the potential also increases to guide current construction practices toward more durable, compatible, and environmentally responsible systems.

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Characterizing abnormal humidity in building mortar using fluorescence imaging technology

Results and discussion

The cement paste of building mortar overlaps independent aggregates to form a unified solid phase as a whole. The pores between the solid phases are the main transmission channels for water and fluorescent molecules, as shown in Fig.1(b). As water migrates, nanoscale rhodamine fluorescent molecules are found to be distributed in the mortar. Rhodamine fluorescent molecules can be divided into two categories. One type of fluorescent molecules solidifies in the hydration product during the hydration process and can be regarded as fluorescent molecules dissolved in chemically bound water, which cannot play a role in fluorescence characterization. The other type is distributed in the solid phase pore structure as water migrates and adheres to the solid phase surface as the water content changes.

The fluorescent molecules in building mortar also conform to the theory of aggregate fluorescence quenching effect. At high humidity, since the fluorescent molecules mainly exist as monomers, at low humidity, the intensity of the polymer-type fluorescent molecules decreases as shown in Figure 2(a). With the increase of humidity, the fluorescence intensity continues to increase, and the fluorescence intensity reaches a peak at a relative humidity of 63% as shown in Figure 1(c) and Figure 2(b).

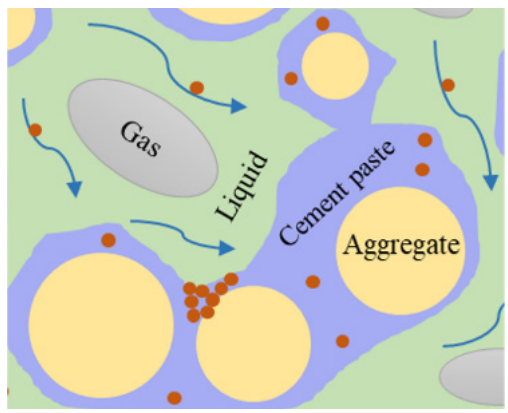

Figure 1. Distribution of fluorescent molecules in mortar.

This technology uses Rhodamine 6G solution as the color-developing solvent for on-site non-destructive humidity detection technology. Figure2(a) shows the change in fluorescence intensity at different solution concentrations. Due to the reabsorption effect of the overlap of the emission spectrum and the tail spectrum of the absorption band, the relationship between the fluorescence intensity and concentration of the solution fluorescence is shown in the Figure 2. The fluorescence intensity is positively correlated with the concentration at low concentrations and negatively correlated with the concentration at high concentrations. The fluorescence intensity of the rhodamine solution is high at 500 ug/mL, and as the concentration continues to increase, the fluorescence intensity shows a negative correlation trend.

The effect of different relative humidity on fluorescence intensity is mainly reflected in that the intensity of fluorescent molecules increases with the increase of humidity under low humidity conditions. It reaches a peak value in an environment of 65% RH as shown in Figure 2(b). As the humidity further increases, the fluorescence intensity gradually decreases. In a 95% RH environment, its fluorescence intensity is lower than that in a dry state. The sensitivity of fluorescent molecules to temperature is obvious. The results of the study on the effect of temperature on the change trend of fluorescence intensity show that the fluorescence intensity is relatively low at low temperatures. This phenomenon is mainly due to the low activity of fluorescent molecules at low temperatures, so the fluorescence intensity is low. As the temper-

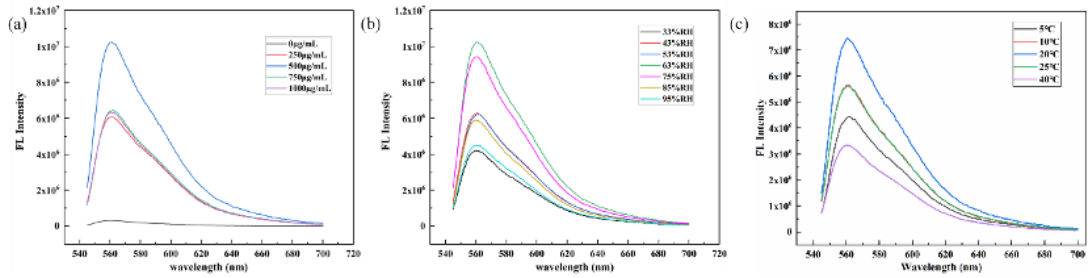

Figure 2. Fluorescence Molecular Characterization of Humidity Evolution. (a) Fluorescence intensity at different concentrations. (b) Fluorescence intensity at different relative humidity. (c) Fluorescence intensity at different temperature

ature increases, the molecular activity gradually increases, and the fluorescence intensity reaches a peak at 20°C, as shown in Figure 2(c).

The fluorescent molecules in building mortar also conform to the theory of aggregate fluorescence quenching effect. At high humidity, since the fluorescent molecules mainly exist as monomers. As the humidity decreases, the fluorescent molecules change from monomers to dimers and polymers. Under low humidity, the intensity of polymer fluorescent molecules decreases due to the aggregate fluorescence quenching effect as shown in Figure 3(a).

Based on the humidity evolution monitoring results of the building exterior wall, a colorimetric diagram of fluorescence intensity at 0% RH, 33% RH, 65% RH and 95% RH was drawn. As shown in Fig.3(b), the fluorescence intensity difference of cement-based materials under low humidity is small. In the range of 33% RH-65% RH, the fluorescence intensity is significantly enhanced, and in the humidity range above 65% RH, the fluorescence intensity gradually decreases. The fluorescence intensity reaches a peak at a relative humidity of 65%.

This technology focuses on the aggregation annihilation effect to solve the problem that the fluorescence intensity of fluorescent molecules is relatively low at low and high humidity. Experiments show that the fluorescence intensity is lowest at 95% RH, and the fluorescence intensity is even lower than that in the dry state. Fluorescence sensing technology can be applied to microscale research on civil engineering materials and can be used to monitor moisture evolution trends in the field of cement-based materials.

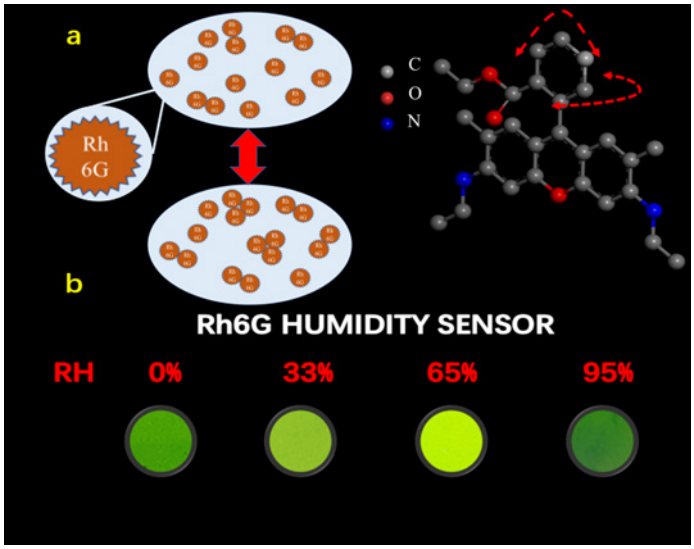

Fig.3 The fluorescent molecules of aggregate fluorescence quenching effect. (a) Structure and Aggregation of Fluorescent Molecules. (b) Fluorescence intensity at different relative humidity.

Abstract
The durability of cement mortar in long-term service under complex service environment is the key factor that determines its service life. Long-term high humidity is an important reason for durability attenuation. This study proposes a fluorescence imaging technology for non-destructive characterization of abnormal humidity in building mortar. The results show that the optimal concentration of fluorescent molecules in building mortar is 500ppm. The fluorescence intensity of fluorescent molecules is the highest at 65% relative humidity. Based on the aggregation caused quenching effects theory, a color card between fluorescence intensity and relative humidity was established. Considering the influence of temperature, the influence of temperature on the evolution of fluorescence intensity was analyzed. This technology realizes on-site non-destructive detection of the location of humidity anomalies and provides guidance for the repair of building mortar defect locations.

Keywords
In-situ non-destructive characterization, fluorescence imaging technology, aggregation caused quenching effects

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Stucco Weathering by Magnesium Sulphate: Effects on Gypsum and Dolomitic Lime Interaction

Historical stucco decorations have defined the appearance of interiors and façades for centuries, offering invaluable insights into past working techniques, regional characteristics, and material use. The interdisciplinary analysis of these artifacts also highlights important aspects of object history and restoration measures that contribute to the preservation of these wall decorations. This presentation will focus on the use of dolomitic lime mortars and the admixture of gypsum in stucco work, examining the weathering processes triggered by their interaction and the formation of magnesium sulphate. While dolomitic lime has been well studied for masonry mortar in North and South Tyrol, recent research reveals its use in stucco decorations and wall paintings, traced back over several centuries in Tyrol and beyond.

The deterioration of mortars is primarily attributable to the formation of deleterious salts, particularly magnesium sulphate in dolomitic lime mortars. The reaction is initiated by the interaction between magnesium ions in dolomitic lime and sulphur dioxide (SO2) present in the atmosphere or other sulphate sources. The presence of moisture facilitates this reaction. Concurrent with the formation of magnesium sulphate, gypsum (CaSO4*H2O) is produced during the reaction with calcium ions present in dolomitic lime.
Three processes are relevant for the formation of magnesium sulphate, with process 3) being of central importance for the present study.

1. Formation of magnesium sulphate by reaction of dolomitic lime with SO2 from the air and moisture
2. Formation of magnesium sulphate by the reaction of dolomite-containing aggregate, with a primary or secondary sulphate source from the binder and water
3. Formation of magnesium sulphate by the reaction of dolomitic lime, gypsum and water

The repeated crystallization and dissolution of deleterious salts in the pore space, as well as volume changes due to hydration processes depending on temperature and humidity, lead to crystallization and hydration pressures in the mortar, resulting in a significant cracking effect. Figure 1a presents a detailed view of the damage to the baroque stucco work on the façade of the Helblinghaus in Innsbruck, Austria, executed by Anton Gigl (about 1730). The stucco composition consists of dolomitic lime with a substantial gypsum content. The material structure of the sample (Figure 1b) of dolomitic lime-gypsum mortar with a dolomitic lime layer was selected as an example for laboratory-based simulations of the damage pattern.

The aim of the programme was to reproduce the stucco mass and then subject fragments of it to repeated cycles of wetting and drying to simulate the environmental effects on a façade. A series of tests with different mortar mixes and different storage conditions, such as temperature, humidity and weathering cycles, were carried out to investigate the underlying mechanisms and to obtain an explanation for the formation of magnesium sulphate and its distribution in the stucco structure as observed in the historical samples.

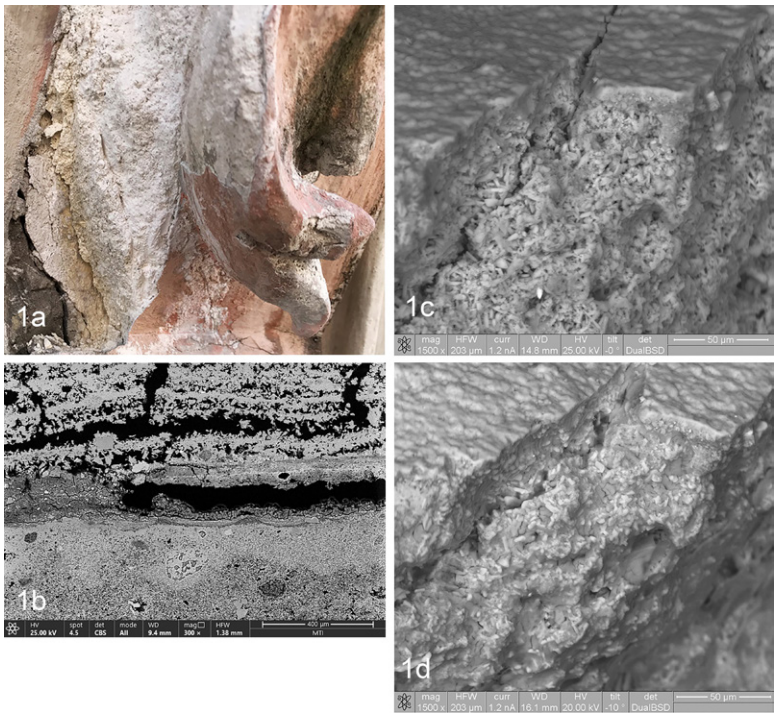

Figure 1: Flaking damage to the stucco on the facade of the Helblinghaus in Innsbruck, Austria (1a). Comparison of SEM images in BSE mode of the historical stucco decoration (1b) and a stucco fragment from the experiments on the reproduction of dolomitic lime-gypsum mortars with a dolomitic lime layer and the formation of magnesium sulphate (1c). Note the more diffuse and denser areas identified as magnesium sulphate (arrow) in the matrix after 3 months of treatment with serveral cycles of wetting and drying (1d).

The mineralogical composition of the raw materials and the dolomitic lime-gypsum mortar is determined at fixed time points using X-ray diffraction (XRD). Differential thermal analysis (DTA) in combination with thermogravimetry (TG) is used to quantify the mineral phases. The texture of the mortars and their compositional characteristics are analyzed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

It was observed that magnesium sulphate penetrated into the mortar matrix at the fracture points within a very short time (Figure 1c and 1d). After serveral cycles within 3 months, the magnesium sulphate penetration was very advanced. In addition, the matrix between the euhedral gypsum crystals and the pores of the stucco mass are filled with magnesium sulphate, comparable to the studied status quo in the historical samples. Besides to efflorescence on the surface and the formation of salts in cracks that widen over time, the plaster mortar near the surface is infiltrated and breaks up.

The following question was derived from these observations:
The chemical composition of stucco mortar made from dolomitic lime and gypsum creates the basis for the formation of magnesium sulphate. Which chemical and physical mechanisms lead to the formation of this salt?

This study aims to provide first steps in the understanding of the damage mechanisms and dynamics of dolomite-lime-gypsum mortar mixtures in the presence of magnesium sulphate and moisture and drying and wetting cycles. By investigating these processes, the goal is to develop solutions to the challenges of preserving historic stucco decorations. Particularly in the case of desalination using compresses, where water is introduced into the structure.

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Laboratory and on-site assessment of durability assessment of natural hydraulic lime plasters with encapsulated crystallization inhibitor

1. Introduction

Plasters and renders in historic buildings are often damaged by salt crystallization, because of their relatively low mechanical strength and their location at the surface of the wall, where evaporation and salt accumulation take place. Current solutions to provide plasters and renders with a better resistance with respect to salt decay are mostly based on the use of stronger binders, such as cement, or of water repellent additives. Unfortunately, both these solutions show often a low compatibility with the materials used in historic buildings.

In the past decade, research has been carried to improve the durability of plasters against salt damage by the use of crystallization inhibitors (e.g.[1-2]) Crystallization inhibitors are ions or molecules able to delay crystal nucleation and growth of the crystal by preferentially adsorbing on specific crystal faces. Sodium ferrocyanide (NaFeC) is a well-known inhibitor of sodium chloride. Past research has shown that NaFeC, is able to provide hydrated lime-based mortars with an improved resistance to salt decay[3]. However, leaching of this water-soluble inhibitor may compromise its effect in time. Recently, encapsulation of NaFeC in chitosan-calcium alginate capsules was proven effective to control the release of the inhibitor in mortar[4]. In this paper, the durability of a natural hydraulic lime plaster with encapsulated NaFeC crystallization inhibitor is discussed based on the results of laboratory accelerated salt weathering test and monitoring of test panels applied on site.

2. Assessment of durability in laboratory

For the preparation of the plasters natural hydraulic lime (NHL) by St Astier) with quartz sand in 1:3 volume proportion were used in the preparation of the plasters. Plaster specimens with NaFeC inhibitor directly mixed in the mass (NHL-F) and with chitosan-calcium alginate capsules containing the NaFeC inhibitor (NHL-CsCA-F) were prepared; as reference, plasters without inhibitor (NHL-R) were also prepared. The inhibitor and the capsules containing the inhibitor were added during mortar preparation, in such a way to obtain 1 % NaFeC content (as % of the binder weight). For details on capsules production and inhibitor content, please see. The fresh and hardened properties of the plasters are summarized in Table 1 (see 4 for more details).

For the assessment of the durability of the plasters to salt crystallization, cylindrical specimens (5 cm diameter) were prepared; these were composed of a 3 cm thick stone substrate and a 2 cm plaster layer which was applied on top of the substrate. Maastricht limestone, with a porosity of 50% v/v and a mean pore size of 30 µm[5] was used as the substrate.

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1 Granneman et al. 2019.
2 Lubelli et al. 2010.
3 Granneman et al. 2019.
4 Kamat 2024.
5 Nunes et al. 2021.

Property	NHL-R	NHL-F	NHL-CsCA-F
Workability (mm)	165.67 ± 0.9	172.33 ± 3.1	164 ± 1.4
Compressive strength (MPa)	0.42 ± 0.08	0.39 ± 0.07	0.62 ± 0.8
Porosity (vol %)	21.83 ± 0.36	22.35 ± 0.27	22.37 ± 0.6
Bulk density (g ml^{-1})	2.03 ± 0.01	2 ± 0	1.99 ± 0.02
Water abs coefficient (g m^{-2} $s^{-0.5}$)	159	147	156

Table 1. Properties of plasters without inhibitor (NHL-R), with inhibitor mixed in the mass (NHL-F), and with encapsulated inhibitor (NHL-CsCA-F)

The procedure used for the assessment of the durability to salt decay is based on the RILEM 271-ASC recommendations[6], and was carried out in two subsequent stages: 1. Accumulation stage, in which 10 % NaCl solution was introduced in the specimens in an amount equal to the capillary moisture content of the stone substrate, followed by drying of the specimens at at 40°C/15% RH until 80% of the water had evaporated. 2. Damage propagation stage, during which specimens were subjected to repeated crystallization/dissolution cycles of the salt in the specimens, induced by temperature and RH changes. Damage was photographically assessed during the test; at the end of the propagation phase, the specimens were brushed and the damage quantified in terms of material and salt loss and efflorescence. The amount of NaFeC leached out was calculated based on the measurement of the concentration of Fe(II/III) ions assessed by Inductively coupled plasma-optical emission spectroscopy (ICP-OES) (see 4 for details). The results of the accelerated weathering test clearly show that the inhibitor, either directly mixed in or in the encapsulated form, clearly reduces the amount of material loss with respect to the refence mortar (Figure 1). Besides, the amount of inhibitor leaching out of the specimens is 30% lower for NHL-CsCA-F mortar than for NHL-F mortar. A slightly higher amount of salt efflorescence is observed in plasters containing the inhibitor (see for details).

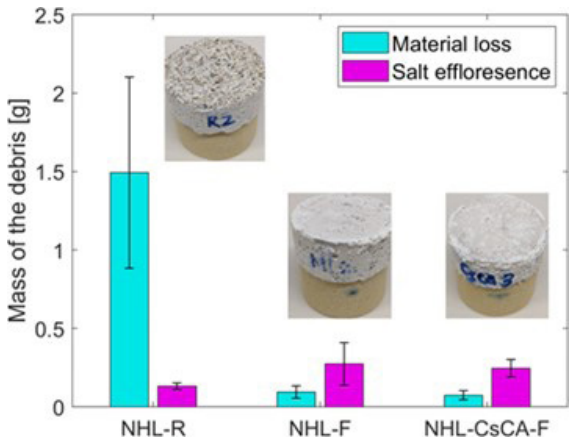

Figure 1. Material loss and salt efflorescence brushed from the surface of the specimens at the end of the propagation stage

3. Assessment of durability on test panels on site

The durability of the NHL plaster with encapsulated inhibitor (NHL-CsCA-F) was assessed on test panels applied on a building (St. Nicolaas church in Brouwershaven, NL) affected by high salt (NaCl) and moisture load from rising damp. In this case, because of the time consuming work needed for the preparation of the capsules, capsules were added only to the inner layer of the plaster (1 cm thick); in the outer layer (1 cm thick) no inhibitor was used. Another panel with NHL mortar without inhibitor (NHL-R) was used as reference.

The assessment of the damage was carried out visually and by assessing the moisture content in the plaster and the masonry after after about 1.5 years from the application. After 1.5 years no visible damage is visible to both the plasters, despite a high salt and moisture load; therefore, more time is needed to draw definitive conclusion on this onsite test. However, it is interesting to notice that no blue discoloration (due to formation of Prussian blue), an earlier observed problem in plasters with mixed-in NaFeC, is visible in the panel with encapsulated inhibitor. This suggests that encapsulation of the inhibitor can not

6 Lubelli et al. 2023.

only reduce leaching of NaFeC[7] while still providing an improved durability to salt decay, but possibly also reduce or avoid the negative side-effect of blue discoloration. Further research on a longer time span is on-going to further validate these conclusions.

Acknowledgements
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7 Lubelli et al. 2023.

Topic 8

Preservation. Consolidation materials and techniques. Development of new products. Preventive conservation

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Comparative study of bio-additives' performance in lime-based mortars

1. Introduction

The implementation of the “green constructions” configuration plan requires the discovery of sustainable with zero-carbon footprint building solutions . A feasible answer to the specific research, has been given since antiquity, when natural, abundant and eco-friendly biomaterials (like straw, wood fibres or seashell particles) were incorporated into clay and lime-based mortars to improve their volume stability and mechanical strength characteristics. Such inclusions have been detected in many Greek monuments since 300 BC, involving structures from archaeological sites (like the one of Dion) and palaces, castles and tombs (such as the Macedonian tomb C located in Pella) . Nowadays, the return to the bio-reinforcing techniques could contribute to the reduction of the environmental pollution, while minimizing the mineral resources dependence and conservation cost.

The bio-additives’ performance in mortar matrixes is affected by many factors related to their morphology and chemical composition. More specifically, their hydrophilic character defines the water demand of the composite, while their shape, diameter, length and surface characteristics, such as their roughness, influence their dispersion in the mortar mixtures and adhesion with the paste[1]. Additionally, many chemical and hydrothermal treatments have been developed to alleviate the bio-fibres chemical compounds concentration and therefore their surface properties[2].

In the context of the restoration methods, the main concern is focused on the compatibility of the repair mortars with the substrate. To achieve this, the restoration solutions should display similar physical, mechanical and hydrothermal properties with the existing traditional materials, ensuring the durability and lifespan of the monuments and historic edifices[3].

2. Materials and methods

The aim of the present research was to evaluate the performance of biomaterials with diverse chemical composition (different species) and geometry-morphology (fibres, powders or bio-solutions) in lime-based mortars and simultaneously the assessment of the treated bio-fibres action compared to the natural ones. For these purposes, 9 lime-pozzolan (L-) mortar mixtures were produced including an unreinforced-reference one (-R) and 8 reinforced mortar samples with black pine wood fibres [natural (-wn) or hydrothermally treated (-wh) or chemically treated with siloxane (-ws), with siloxane and nano-silica (-wsn)] or black pine wood powder (-wp) or pine tree resin (-r) or rice husk fibres (-f) or a combination of them (-rf). All fibre and powder shaped bio-additives were incorporated into the mortar matrix in a dry state at a stable addition rate of 1.5% v/v (volume of bio-additives per mortar volume), while the tree resin was inserted at a 1.5% w/w (resin dry weight per binder weight) addition portion after it was dissolved in ethanol solution (10 g of tree resin mixed with 33 ml ethanol). For the mortar components, air lime and natural

1 Kampragkou, Stefanidou 2025.
2 Ajouguim et al. 2019.
3 Loureiro et al. 2020.

pozzolan were utilized as binders in a 1/1 mixing proportion by mass, natural siliceous sand (river origin) with 0-4 mm granulometry was used as aggregates in a binder/aggregate ratio of 1/2.5 by mass and the water/binder ratio was stable at 0.74. It should be noted that a stable portion of 1% w/w weight per binder weight, superplasticizer was implemented when it was necessary (in the bio-reinforced mixtures) to achieve the desired workability of 15 ± 1 cm (based on EN 1015-3). For the accomplishment of the experimental procedure prismatic (4 x 4 x 16 cm3) and slab-plate (20 x 20 x 2.5 cm3) mortar specimens were produced.
After 90 hardening days (including ageing for 28 days in humid conditions and then hardening at indoor environment), all mortar samples were assessed for their open porosity and apparent specific gravity values (based on RILEM CPC11.3), while their capillary absorption (according to EN 1015-18), flexural tensile strength (based on EN 14651), dynamic modulus of elasticity (according to EN12504-4) and flexural and compressive strength (based on EN 1015-11) were determined. The analysis was completed with the designation of the specimens' water vapor resistance factor μ (in accordance with the specific ageing specifications and experimental procedure described at the standards EN 1015-19 and ISO 12572) and thermal conductivity coefficient λ (based on EN 12667) at two mean heating temperatures, namely at 10C and 20C.

3. Results and discussion

Evaluating the experimental results, it seemed that the implementation of bio-additives (regardless of their species, geometry and treatment) into the lime-based mortar matrix led to lighter final products, with lower capillary absorption values and better hygrothermal properties (in most cases), in terms of the thermal comfort and good air regulation, compared to the reference case. Although, they showed reduced mechanical strength values (except the 15.6% increase in the flexural strength of the Lwh case) in comparison to the LR samples, better post cracking behavior when fibre shaped biomaterials (regardless of their species and treatment) were utilized.
Comparing the species' performance, the wood fibre and rice husk fibre enhanced samples exhibited similar physical and mechanical characteristics, with the rice husk reinforced ones to display lower thermal conductivity values. Moving to the pine tree behavior in lime-based matrix, it appeared that it contributed to declined porosity values and water capillary absorption tendency (at both Lr and Lrf studied cases) compared to the reference samples with the significant 9 times C (capillary absorption coefficient) reduction of the pure tree resin reinforced case (Lr). Nevertheless, their mechanical performance was impaired, except for the improved residual flexural tensile strength of the Lrf case compared to the Lf samples. Finally, in contrast with their porosity values, the tree resin enhanced specimens presented decreased λ and μ values contrary to the LR specimens, revealing the tree resin ability to block the heat transfer and meanwhile provide water vapor transmission pathways inside traditional matrixes, so to alter the pores size and interconnectivity.
The transition from fibre to powder wood particles was accompanied by an improvement in the thermal behavior of the lime-based mortars and a blocking in the capillary pores connection. In contrast, the fibre-shaped enhanced mortars distributed better mechanical and μ records. Moreover, regarding the treated wood fibre performance, hydrothermal treatment boosted the flexural and compressive strength of the lime-based mortars.

4. Conclusions

To sum up, the incorporation of bio-additives in lime-pozzolan mortar mixtures affected the physical, hygrothermal and mechanical properties of the specimens, with this influence to be related with their chemical composition (kind and treatment) and morphology (fibre or powder shape). The choice of the best bio-reinforcing technique should be determined after the thorough evaluation of the desired final product characteristics and the pursuit of the compatibility between the repair mortar and the substrate in restoration cases. Therefore, the utilization of biomaterials in the construction sector could be attrib-

uted to the formation of eco-friendly and low-cost materials with applications in renders/plasters and in enhancing hygrothermal properties. Continuing the traditional techniques of bio-reinforcing mortars by advancing the properties using new techniques, seems a safe way for compatible and durable conservation.

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Multifunctional coatings with water-oil repellence and photocatalytic properties for lime-based mortars

1. Introduction

Heritage structures are highly susceptible to deterioration caused by salt accumulation, moisture infiltration, microbial growth, graffiti, and various environmental pollutants. The limitations of traditional cleaning and waterproofing techniques often fall short in adequately protecting these buildings. This study introduces the use of Bi_2O_3-ZnO (8/92) photocatalyst combined with non-ionic dispersants (TritonX-100, Tween20, and Brij35) in superhydrophobic (W) and hydro-oleophobic (O) solutions. These formulations are applied to both lime and lime-cement mortars to evaluate their repellency and photocatalytic capabilities.

2.Materials and methods

The coatings are developed using solvents supplied by TECNAN, featuring ceramic nano-oxides that impart water-oil repellent properties. The Bi_2O_3-ZnO (8/92) nanoparticles, crucial for the coatings, are synthesized through flame pyrolysis at the Lurederra Technology Centre. Non-ionic dispersants such as TritonX-100, Tween20, and Brij35 are incorporated to ensure a uniform distribution of nanoparticles throughout the mixture. The specific compositions of these coatings are detailed in Table 1.

Prior to application, each mixture undergoes magnetic stirring for 45 minutes to achieve homogeneity. The coatings are then applied to prismatic mortar specimens measuring 5×5×2 cm, which are subsequently left in a horizontal position for 24 hours. The effectiveness of the coatings in repelling water and oil is quantified by measuring the contact angles of water and hexadecane. The assessment is performed using a Dataphysics OCA 15EC instrument, where 3 µL droplets are dispensed at a rate of 1 µL/s, and the behaviour of the droplets is monitored over a 10-second period. Multiple measurements are taken to ensure reliability and to calculate average values.

Photocatalytic efficiency is evaluated under simulated sunlight conditions provided by a 300 W Osram Ultravitalux lamp in a laminar flow reactor, in accordance with ISO 2016 standards. The concentrations of NO and NO_2 are continuously monitored using an Environment AC32M chemiluminescence detector, providing critical data on the photocatalytic activity of the coatings.

3. Results and discussion

Contact angle tests with water and hexadecane indicated trends that are consistent with previous studies[1]; however, no measured angles exceeded 90 degrees. This is likely attributed to the high porosity of the mortars, which facilitates the absorption of droplets. Surfaces treated with the superhydrophobic (W) formulation exhibited increased hydrophobicity, whereas those treated with the hydro-oleophobic (O) solution demonstrated enhanced oleophobic properties.

Photocatalytic tests of the Bi2O3-ZnO (BiZn) nanoparticles under both solar and strictly visible light

1 Tena-Santafé 2023, 1412.

Samples	Photocatalyst (1%)	Dispersant (%)	Solvent
BiZn-ref-W	Bi2O3-ZnO 8/92	-	Water-repellent
BiZn-Tw1-W	Bi2O3-ZnO 8/92	1% Tween20	Water-repellent
BiZn-Tw3-W	Bi2O3-ZnO 8/92	3% Tween20	Water-repellent
BiZn-Tr1-W	Bi2O3-ZnO 8/92	1% TritonX-100	Water-repellent
BiZn-Tr3-W	Bi2O3-ZnO 8/92	3% TritonX-100	Water-repellent
BiZn-Bj1-W	Bi2O3-ZnO 8/92	1% Brij35	Water-repellent
BiZn-Bj3-W	Bi2O3-ZnO 8/92	3% Brij35	Water-repellent
BiZn-ref-O	Bi2O3-ZnO 8/92	-	Water and oil repellent
BiZn-Tw1-O	Bi2O3-ZnO 8/92	1% Tween20	Water and oil repellent
BiZn-Tw3-O	Bi2O3-ZnO 8/92	3% Tween20	Water and oil repellent
BiZn-Tr1-O	Bi2O3-ZnO 8/92	1% TritonX-100	Water and oil repellent
BiZn-Tr3-O	Bi2O3-ZnO 8/92	3% TritonX-100	Water and oil repellent
BiZn-Bj1-O	Bi2O3-ZnO 8/92	1% Brij35	Water and oil repellent
BiZn-Bj3-O	Bi2O3-ZnO 8/92	3% Brij35	Water and oil repellent

Table 1. Compositions considered of multifunctional coatings for the titanium and bismuth experiments

conditions revealed diminished effectiveness when exposed only to visible light, underscoring the nanoparticles' higher responsiveness to ultraviolet light. The BiZn nanoparticles achieved a 70% efficiency in NO removal, and the selectivity for NO_x versus NO removal under solar light was an impressive 95.5%. This demonstrates the nanoparticles' substantial capability to significantly reduce NO concentrations while minimally producing the harmful intermediate NO_2, primarily resulting in the formation of non-toxic nitrate. Figures 1(a) and 1(b) illustrate these photocatalytic results for NO and NO_x removal.
Notably, lime-based substrates outperformed lime-cement ones, largely due to their rougher texture. Alterations in dispersant concentrations significantly boosted NO/NO_x removal rates, corroborating zeta potential and particle size measurements reported in earlier studies1. In some instances, removal rates exceeded 30%, a marked improvement over the typical 10–15% removal rates observed with similar coatings applied to stone surfaces1. This enhanced performance is likely influenced by two primary factors: (i) the substrate's alkalinity, which facilitates the reduction of nitrogen oxides through disproportionation processes, and (ii) the increased porosity of the mortars, which aids in the adsorption and subsequent removal of nitrogen oxides.

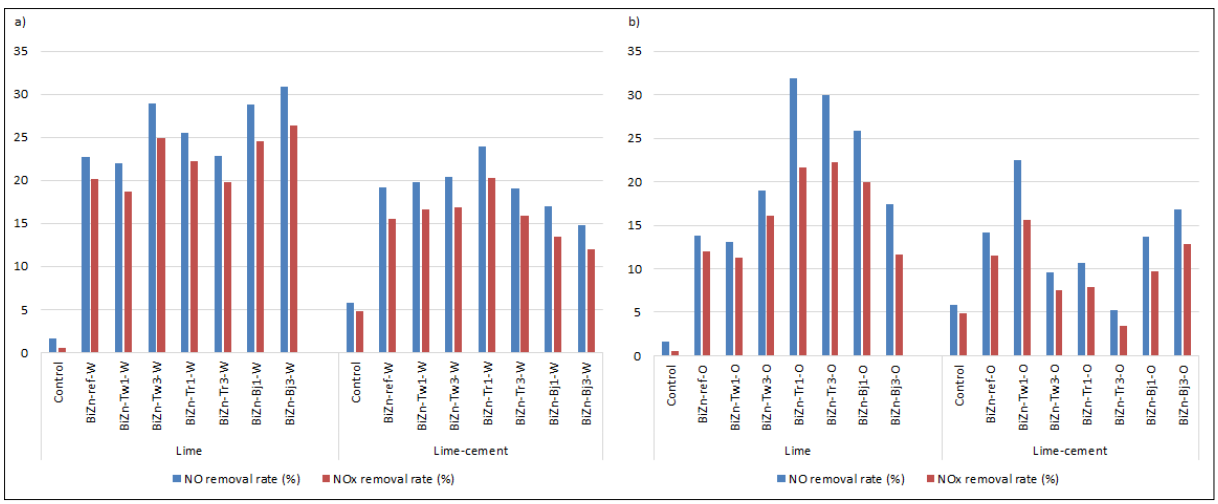

Figure 1. NO and NOx BiZn removal rates (solar light): (a) water repellent (W), and (b) oil repellent (O) solvent.

4. Conclusions

Multifunctional coatings incorporating 3D superhydrophobic and oleophobic inorganic solvents alongside bismuth-zinc photocatalysts and non-ionic dispersants, are engineered for application on lime and lime-cement substrates. These dispersants meticulously selected to prevent particle agglomeration, significantly enhancing the photocatalytic efficiency of the coatings. The specialized solvents confer superior water and oil repellence to the mortars, ensuring robust performance under solar illumination, actively degrading pollutants and contributing the coatings' overall effectiveness.

Acknowledgments

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Optimizing the Use of Basalt Fiber in Lime-Based Mortars for Heritage Applications

1. Introduction

The reinforcement of lime-based mortars with fibres has increasingly attracted attention within heritage restoration due to its potential to enhance mechanical properties, durability, and workability while preserving compatibility with historic structures. Among various fibres, basalt fibre stands out as particularly promising due to its natural origin, exceptional mechanical properties, and resistance to environmental degradation[1]. Previous research has demonstrated that basalt fibre incorporation effectively mitigates cracking, improves flexural strength and durability, and influences the workability of cement-based[2-3], and natural hydraulic lime-based[4-5] mortars. These effects largely depend on the fibre dosage, length, and distribution within the matrix. However, despite these promising findings, research exploring the performance of basalt fibre in air lime-based mortars remains limited, underscoring area critical research gap.
To address this gap, this study investigates the influence of varying amounts of basalt fibre reinforcement in both air lime-based and NHL-based mortars including pozzolanic additions (volcanic ash and silica fume). Fresh-state properties, mechanical performance and microstructural characteristics of these mortars are systematically evaluated, aiming to provide insights into their suitability for heritage conservation applications.

2. Materials and Methods

2.1 Materials

The mixture designs are presented in Table 1. The lime-based mortars were formulated using natural hydraulic lime (NHL-5) and calcitic air lime (CL-90) as binders, combined with standard silica sand as aggregate. Silica fume and volcanic ash were introduced as pozzolanic materials to enhance mechanical properties. Basalt fibres were included at two dosage levels: 1% and 4 % by weight of lime. A polycarboxylate-based superplasticizer (SP) was used as needed to ensure adequate fludity, while maintaining a constant water content.
All dry components were thoroughly mixed to ensure homogeneity before gradually adding water. Mixing was carried out at low speed for 90 seconds. The fresh mortar was subsequently cast into cylindrical moulds. Air lime-based mortar samples were cured under controlled laboratory conditions (20°±2°C, 45±5% RH), while NHL-based mortars were cured in a curing chamber at high RH (20±2°C, 95±5% RH).

1 Villanueva et al. 2024.
2 Wang et al. 2024.
3 Guler, Akbulut 2023.
4 Santarelli et al. 2014.
5 Iucolano, Liguori, Colella 2013.

	NHL	Air Lime	Silica Sand	Silica Fume	Volcanic Ash	Basalt Fibre	SP (%)	Water/ Dry mix	Flow Table (mm)	Water Retention (%)	Compressive Strength (MPa)			Weight Loss (%)	
											7th day	28th day	91st day	200-600°C	600-900°C
N0	1	-	3	0,1	0,1	-	0,2	0,15	180	94,88	2.2 ± 0.2	6.2 ± 0.4	8.4 ± 0.8	2,72	4,44
N1	1	-	3	0,1	0,1	0,01	0,2	0,15	174	90,51	2.1 ± 0.2	6.0 ± 0.4	7.8 ± 0.9	2,25	4,33
N4	1	-	3	0,1	0,1	0,04	0,3	0,15	175	94,44	3.0 ± 0.3	7.8 ± 0.6	11.4 ± 0.2	2,13	3,61
A0	-	1	3	0,15	0,15	-	-	0,25	185	94,24	0.3 ± 0.1	0.5 ± 0.01	1.7 ± 0.4	2,75	8,3
A1	-	1	3	0,15	0,15	0,01	-	0,25	190	93,39	0.4 ± 0.02	0.8 ± 0.06	1.8 ± 0.1	1,98	12,43
A4	-	1	3	0,15	0,15	0,04	-	0,25	193	95,16	0.7 ± 0.03	1.6 ± 0.1	1.5 ± 0.2	2,24	10,23

Table 1. Mixture proportions, fresh state analyses, compressive strength results, and TGA data.

2.2 Experimental Methods

Fresh-state and hardened-state properties of mortar samples were evaluated. In the fresh state, fluidity[6] and water retention[7] tests were conducted. Compressive strength was assessed at 7, 28, and 91 days of curing. Porosity and pore size distribution were analysed at 91 days using Mercury Intrusion Porosimetry (MIP) within a pressure range of 0.0015 to 207 MPa. Thermogravimetric Analysis (TGA) was performed at 91 days, from 35°C to 1000°C under a nitrogen atmosphere. Microstructural features were examined by Scanning Electron Microscopy (SEM).

3. Results

In NHL-based mortars, basalt fibre addition caused a reduction in slump values (Table 1). The necessity for superplasticiser increased with the higher fibre content to maintain optimal slump, consistent with findings from previous studies3. However, air lime-based mortars showed the opposite trend, with increased fibre content enhancing flowability. Water retention slightly decreased at 1% fibre content but was restored close to reference values at 4% fibre content.

Compressive strength peaked at 91 days, improving with basalt fibre addition (Table 1). NHL samples demonstrated enhanced strength across all ages, notably at 91 days. Basalt fibres significantly accelerated early strength development in air lime-based mortars, with strength gains up to threefold at early stages, although the rate of strength gain slowed after 28 days.

SEM analysis revealed a denser and more uniform microstructure in NHL-based mortars, correlating with approximately 10% lower porosity compared to air lime-based mortars. The basalt fibres were uniformly distributed without compromising structural integrity (Figure 1a). In contrast, air lime mortars exhibited weaker binder-fibre interaction, yet fibres effectively mitigated cracking by bridging the cracks (Figure 1b).

TGA indicated hydration (200–600°C) and carbonation (600–900°C) processes (Table 1). Increased basalt fibre content reduced hydration-related weight loss due to modified water retention and the creation of small voids at the fibre-binder interface[8]. Higher fibre content led to reduced carbonation in NHL mortars, whereas fibre incorporation enhanced carbonation in air lime mortars, likely due to their inherently more porous structure.

4. Conclusions

This study demonstrated the effects of basalt fibre reinforcement on air lime and NHL mortars. Basalt fibre addition influenced mortar flowability, reducing it in NHL-based mortars but improving it in air lime-based mortars. Additionally, compressive strength tests revealed that 4% basalt fibre incorporation

6 UNE-EN 1015-3.
7 UNE-EN 83816:2021.
8 Iucolano, Liguori, Colella 2013.

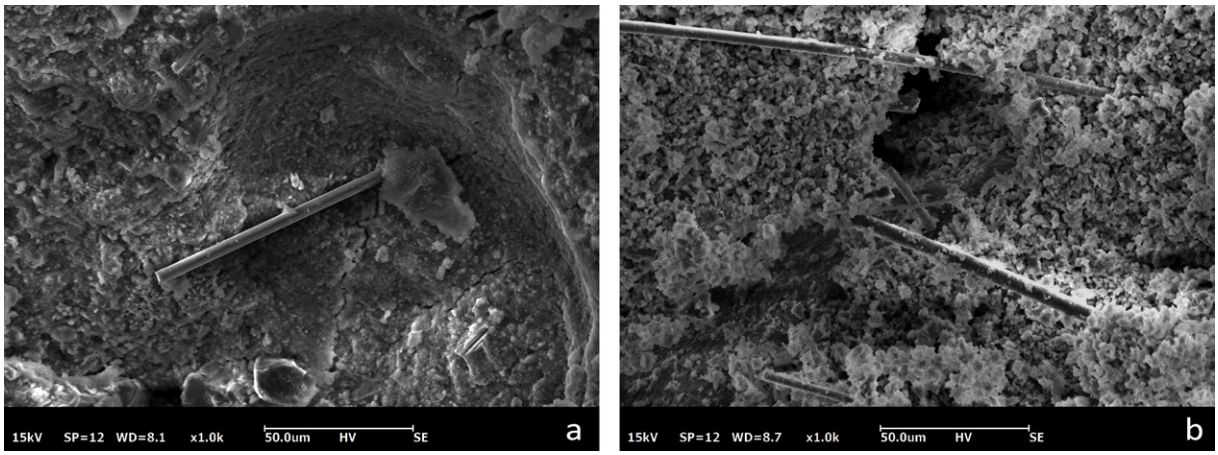

Figure 1. (a) SEM image of sample N4 at 91 days of curing, (b) SEM image of sample A4 at 91 days of curing.

yielded the most beneficial results, significantly enhancing strength and effectively mitigating crack propagation within the mortar structure.

5. Acknowledgements

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FEDERICA PARLATO

Testing of silica-based protective coatings synthesized via sol-gel for earthen surfaces. The case of the Church of San Luís in Granada

1. The climatic dimension in earthen architecture heritage conservation

The historical diffusion of construction systems using earth as a building material in Spain is primarily attributed to the availability of high-quality raw materials, favorable climatic conditions, and its introduction during the period of Muslim rule, followed by the development of various techniques between the 11th and 16th centuries[1].

However, the hydrophilic and porous nature of earth makes tapia structures particularly vulnerable to atmospheric agents. The attempt to counteract the intrinsic weakness of this material has led to the development of multiple technical, material, and formal solutions, primarily aimed at reducing the erosive action of water and limiting the consequent loss of material[2].

Despite the protective measures implemented by traditional construction practices, the preservation of historic earthen architecture is increasingly threatened by changing environmental variables[3]. According to data collected by AEMet, intense rainfall events are becoming increasingly frequent across the Iberian Peninsula, even in areas that were not historically affected[4]. This trend is particularly evident in the Mediterranean region, which, despite having moderate to low average annual precipitation, experiences the most intense rainfall events—a phenomenon that predictive studies indicate will significantly worsen.

The preservation challenges associated with earthen architecture often led to interventions resorting to the replacement of historic material. To avoid such practices—often employed in the conservation and consolidation of earthen heritage—it is crucial to develop innovative solutions (protocols and products) that can mitigate the effects of earth-water interaction, the principal factor responsible for material degradation and erosion.

2. Testing of protective treatments for earthen surfaces

The various research contributions and analyses of treatments for earthen structures, though few in comparison to those for other building materials common in architectural heritage, identify ethyl silicate as the product with the best performance, despite some disadvantages related to the reduction of water

1 The publication "La restauración de la tapia en la Península Ibérica. Criterios, técnicas, resultados y perspectivas", a result of the research project funded by the Ministerio de Ciencia e Innovación (2011-2013), provides an overview of the various types of tapia found in the Iberian Peninsula, the European geographical area with the most extensive presence of tapia-built architecture. Mileto, Vegas 2014.

2 Numerous studies on earthen architecture highlight its extreme vulnerability to water exposure. Minke 2010; Mileto, Vegas 2014; Luo et al. 2020; Beckett C.T.S., Jaquin P.A., Morel J.-C. 2020; Luvidi L., Fratini F. et al. 2021; Progetto RISK-Terra 2019-2021; ISCEAH 2021.

3 Nakhaei Ashtari M., Della Ventura G., Correia M. 2025.

4 A comparison between the map of average annual precipitation and that of average maximum daily precipitation for the period 1981–2010 reveals that, in general, there is no correspondence between the rainiest areas (northern and northeastern parts of the peninsula) and those with higher averages of maximum daily precipitation, exceeding 80–100 mm (Mediterranean area). Maps provided by AEMet (Agencia Estatal de Meteorología) based on data processed by IGN (Instituto Geográfico Nacional).

vapor permeability and the variable reaction that is heavily dependent on environmental conditions[5].
Given the widespread presence of earthen built heritage in Granada and the amplification of issues related to the intensification of heavy rainfall phenomena predicted in this area, the experimentation of innovative products was conducted on the case study of the Church of San Luís, in collaboration with Siltea Srl. The decision was made to test silica-based protective coatings synthesized via the sol-gel process, considered an evolution of the ethyl silicate treatment, to evaluate their effectiveness in terms of the persistence of the water-repellent effect on the material, compatibility, durability, re-treatability, and maintenance of both breathability and appearance of the material.
The sets of material samples were collected from various representative parts of the earthen structure dating from the early construction phase of the church (made of tapia con machones y verdugadas de ladrillo). The characterization of the plaster samples and earthen modules (through optical microscopy on polished sections, chemical-morphological analysis using ESEM-EDS, and quantitative mineralogical analysis by X-ray diffraction) allowed for an in-depth understanding of the material, highlighting both similarities and differences resulting from subsequent interventions and repairs.
The application tests and subsequent accelerated aging cycles through immersion and drying not only allowed for the evaluation of the performance of the two selected formulations but also enabled the establishment of a correlation between the material's behaviour and its composition.

3. Future Perspectives in the conservation of earthen architecture

The positive outcomes of laboratory experimentation encourage further exploration of this product's application. Given the considerable compositional and structural variability of earthen materials, conducting in situ tests would not only allow for monitoring the material's response to real atmospheric conditions over time but also provide a deeper insight into its potential applications. This would facilitate the evaluation of its adaptability to various contexts, potentially expanding its use to other sites characterized by a widespread earthen architectural heritage.

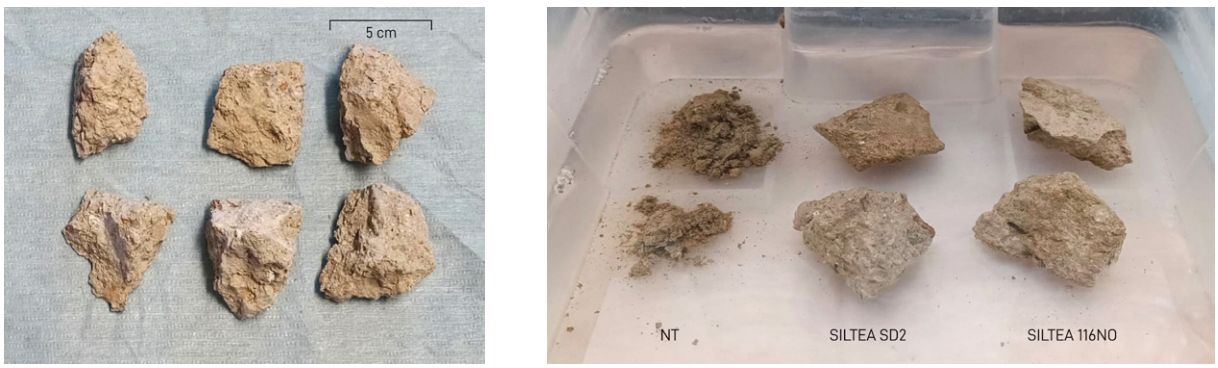

Figure 1. Left: Samples (Series A) before the application of the treatment. Right: Samples (Series A) during the third water immersion cycle. The difference in behavior between treated and untreated samples is clearly visible under the stress induced by the aging cycles

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Effect of natural carbonation on the phase composition and microstructure of natural hydraulic lime-based materials modified by metakaolin

1. Introduction

NHL-based materials demonstrate relatively sluggish development of early mechanical properties in practical engineering. Recent years, extensive research has been conducted by scholars to enhance the performance of NHL. The most direct approach to enhance the early performance of NHL-based materials is to regulate their initial hydration process. Currently, various pozzolanic materials, such as metakaolin, slag powder, silica fume, diatomite and fly ash, have been employed for optimizing the performance of NHL. Research conducted by Grilo et al. demonstrated that metakaolin can improve the strength of NHL mortar[1]. Moreover, high humidity curing conditions favor hydration and pozzolanic reactions. The use of metakaolin considerably enhances the bond strength of NHL-based materials and leads to the formation ettringite, hemicarboaluminate and monocarboaluminate[2]. Slag and silica fume significantly promote the hydration process of NHL-based materials while effectively improving their acid resistance and sulfate resistance[3]. Fly ash modification effectively reduces yield stress and plastic viscosity in NHL grouting material but may result in poor mixability and toughness of mortar [7]. Additionally, diatomite modification increases porosity and water absorption in NHL mortar which is disadvantageous for building applications[4]. The primary impact of metakaolin modified natural hydraulic lime is to alter the composition of hydration-carbonation products, micropore structure during the hardening process, thereby influencing the development of macroscopic performance. This study base on an investigation into metakaolin modified NHL-based materials, and explores phase transformation and microstructure evolution under natural carbonation, elucidate the influence mechanism of environmental conditions on metakaolin modified NHL-based materials.

2. Sampling

The experiment utilized natural hydraulic lime (NHL2) and metakaolin as the raw materials. The NHL, sourced from Saint-Astier Company in France, primarily consists of dicalcium silicate (C2S), Ca(OH)2, with small amounts of CaCO3 and Mg(OH)2. Metakaolin was provided by Inner Mongolia Super New Material Co., Ltd., and is mainly composed of a glassy aluminosilicate phase. ISO standard sand was employed as the sand component in the mortar mixtures.

The four groups of samples were prepared by mixing NHL and metakaolin as follows: NHL2 as the control group, and different proportions of metakaolin and NHL2 (the mass ratio of metakaolin to binder were 10, 20% and 30%, respectively), which were recorded as NHL, M10NHL, M20NHL and M30NHL. The water-to-binder ratio (w/b ratio) was set at 0.55 and the binder-to-sand ratio (b/s ratio) was maintained at 1:3, the binder obotain NHL and metakaolin.

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1 Grilo et al. 2014.
2 Vavričuk et al. 2018.
3 Zhang et al. 2020.
4 Xu et al. 2016.

3. Results and discussion

The compressive strengths (CS) and flexural strengths (FS) of M-NHL mortars at different curing ages and metakaolin dosages are presented in Figure 1. For NHL mortar, the CS and FS are 2.28 MPa and 1.65 MPa at 28 days, respectively, which gradually increase with aging. For M-NHL mortar, both CS and FS increase with longer curing age and higher metakaolin dosages. The CS of M10NHL, M20NHL and M30NHL mortars are 9.49MPa, 13.72MPa and 18.94MPa at 28 days, which are significantly higher than that of NHL mortar. However, it is worth noting that there is a slight decrease in local variations of CS from 14 days to 28 days for M-NHL mortars due to potential instability of hydrate phase during this stage. Additionally, both CS and FS slightly decrease for M30NHL mortar at 180 days. The addition of metakaolin generally exhibits a significant enhancement effect on the mechanical properties of NHL mortar.

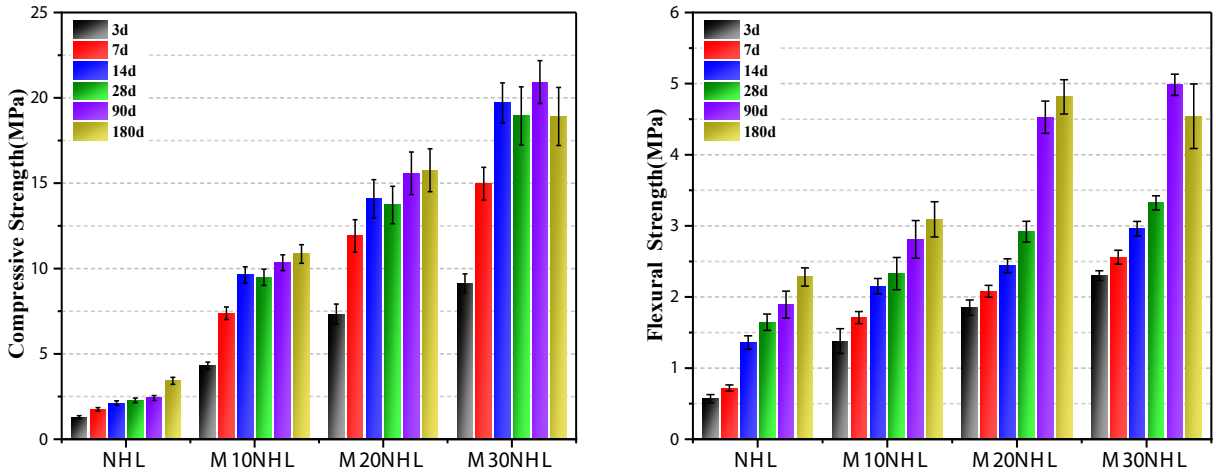

Figure 1. Compressive and flexural strength of M-NHL mortars at various curing ages

The hydration and carbonation product composition of M-NHL hardened pastes at different curing ages are characterized by XRD. For NHL paste, the main phase compositions include C2S, Ca(OH)2, CaCO3 and C-S-H. The diffraction peak intensity of C2S gradually weakens with increasing age until only a small amount remains after 180 days. Overall, the hardening process of NHL can be summarized as follows: water reacts with C2S to generate C-S-H and Ca(OH)2 during its hydration process, and the carbonation reaction occurs between Ca(OH)2 and some C-S-H react with CO2 gas in the presence of water to form calcium carbonate with aging. The main crystal form of calcium carbonate is calcite, with small amounts of aragonite and vaterite present. In addition to the hydration of C2S producing to C-S-H, the pozzolanic reaction between Ca(OH)2 and metakaolin will also produce a large amount of C-S-H in M-NHL pastes. Furthermore, some other phases containing multiple elements (Ca, Al, Si, C, et al) are also formed by the pozzolanic reaction, such as monocarboaluminate(C4AĈH11), calcium aluminate hydrate (C2A(OH)7H6.5, C4AH19 and C3AH6), and strätlingite (C2ASH8), and all phases composition also changes with the different metakaolin dosages and curing ages.

4. Conclusions

Based on the active mineral powder (metakaolin) modified natural hydraulic lime-based materials and the effect of natural carbonation, this study investigated the mechanical properties and products composition. The following conclusions can be drawn: The mechanical strength of M-NHL mortar increases with aging and metakaolin dosage. In M-NHL hardened paste, C-S-H and C4AĈH11 are the primary hydration products in the early stages. C-S-H and C-A-(S)-H occur carbonation reaction at the long age, while C4AĈH11 is more likely to undergo decomposition or transformation into other phases, which is the root cause of the compressive strength decrease slightly from 14 days to 28 days.

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Abstract
The issue of slow early setting and strength development is a common problem faced by natural hydraulic lime (NHL) in both historic building restoration projects and modern construction. This study aims to reveal the phase composition and microstructure of natural hydraulic lime-based materials modified by metakaolin and its effect by natural carbonation. The results demonstrate that metakaolin could promotes the setting times of NHL, and generally exhibits a significant enhancement effect on the mechanical strength. Additionally, the drying shrinkage of NHL mortar can be effectively reduced by adding 10% metakaolin. In terms of hydration products, C4AĈH11 and C-S-H are identified as primary products during the early stages for M-NHL mortars, along with other hydration products such as C-A-(S)-H being formed later on. At longer ages, the carbonation reactions occur primarily with C-S-H and C-A-(S)-H phases, while decomposition or transformation into other phases is more likely for C4AĈH11. Interestingly, when M-NHL mortars with 10% metakaolin, it not only promotes early hydration but also enhances long-term carbonation processes. The significant carbon dioxide uptake effect (~20% wt.%) is also found significant. The pozzolanic effect induced by metakaolin that reduces macropores and refines pore size within M-NHL system, which helps maintain high pore connectivity coefficient as well as effective porosity.

Key words
Natural hydraulic lime; metakaolin; natural carbonation; hydration product; microporous structure

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Comparative Study on the Microphase Composition, Microstructure, and Mechanical Properties of Metakaolin-Modified Aerial Lime under Natural and Accelerated Carbonation Conditions

1. Introduction

Before the invention of Portland cement, aerial lime (AL) was one of the earliest binding materials used in construction, dating back to 10,000 BC. Many historic masonry buildings were constructed using lime-based materials as the main binding component. However, due to long-term natural weathering and human-induced damage, these structures often face deterioration, and in some cases, overall instability or collapse risks. In the restoration of historic buildings, AL is widely used due to its excellent compatibility with original materials. However, its inherent defects, including poor early water resistance, slow strength development, and significant drying shrinkage, limit its direct application in restoration projects[1]. To overcome these issues, researchers commonly incorporate materials like metakaolin (MK), a pozzolanic material, to enhance the properties of AL-based materials[2]. The active SiO2 and Al2O3 in MK can react with CH to form hydration products like C-S-H and C-A-H, thereby improving the mechanical properties and durability of the material[3]. The performance development of pure AL mainly relies on the slow carbonation process, where CH reacts with CO2 to form CaCO3, enhancing the structural strength. However, in the MK-AL composite system, while pozzolanic reactions contribute to performance development, carbonation competes for the calcium source, inhibiting the continuation of pozzolanic reactions, creating a dynamic antagonistic relationship between the two reactions. Moreover, carbonation may further influence the microstructural stability of hydration products, thereby altering the material's final performance. Therefore, this study systematically reveals the competitive mechanisms between pozzolanic and carbonation processes by comparing the microphase evolution, pore structure characteristics, and mechanical property development of MK-AL systems under natural and accelerated carbonation conditions. This provides theoretical support for optimizing the mix design of MK-AL composite systems and enhancing the long-term durability of restoration materials for historic buildings.

2. Sampling and Testing Methods

The raw materials used in this study were AL and MK, sourced from Huiteng Chemical Products Sales Co., Ltd. (Henan, China) and Chaopai New Materials Co., Ltd. (Inner Mongolia, China), respectively. The XRD patterns of these materials are shown in Figure 1(a), where the main mineral phases of AL are Ca(OH)2 and CaCO3, and MK consists mainly of amorphous silica-alumina phases. The median particle sizes of AL and MK are 2.987 μm and 8.464 μm, respectively (Figure 1(b)). Four types of samples (AL, MK10AL, MK20AL, MK30AL) were prepared by replacing AL with MK in different mass ratios (0%, 10%, 20%, 30%), with a water-to-binder ratio of 0.6. After casting, the samples were cured for 3 days and tested for compressive strength under NC and AC (3% CO2) conditions. The phase composition of the hardened pastes was characterized by XRD and thermogravimetric analysis, and the microstructure was observed

1 Oliveira et al. 2024.
2 Gameiro et al. 2014.
3 Gameiro et al. 2012.

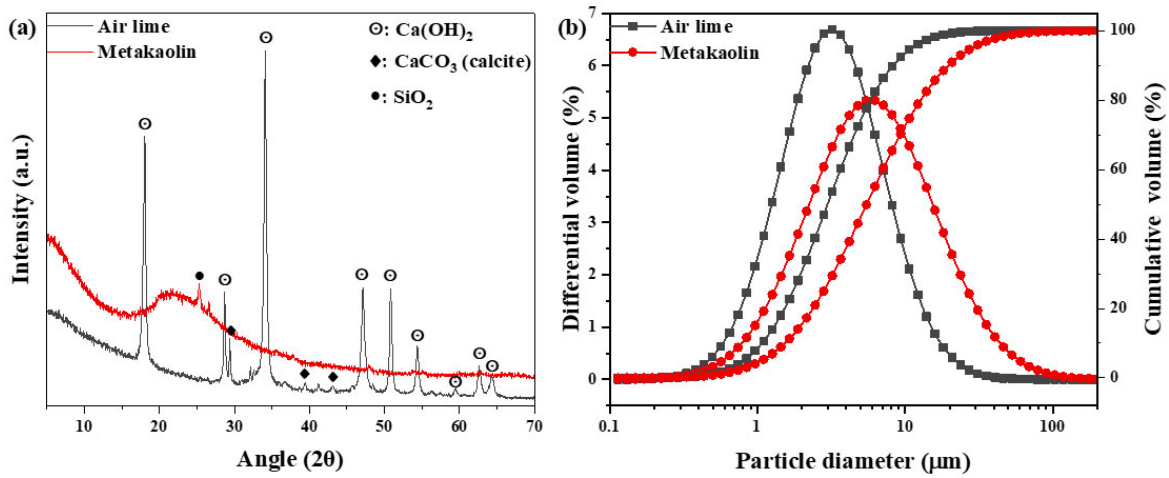

Figure 1. XRD patterns and particle size distribution of aerial lime and metakaolin: (a) XRD patterns, (b) particle size distribution.

using scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP). All samples were appropriately treated before testing to ensure data accuracy and reliability.

3.Results and discussion

Under NC conditions, the incorporation of MK significantly enhancesenhanced the compressive strength of the hardened paste, especially in the MK30AL system, where the formation of products such as Strätlingite, C4AĈH11, and C3AH6, generated from the pozzolanic reaction, improvesimproved the pore structure and greatly increasesincreased compressive strength. At 3 days of curing, the compressive strength of MK30AL reached 7 MPa, primarily due to the pozzolanic reaction between MK and Ca(OH)2. As time progressesprogressed, Ca(OH)2 iswas consumed, further promoting the improvement of pore structure and strength. However, under AC conditions, the increased CO2 concentration acceleratesaccelerated the conversion of CH to CaCO3, competing with the pozzolanic reaction. Under AC conditions, the compressive strength of MK-AL systems shows an initial increase followed by a decreaseinitially increased and then decreased, especially at 28 days, wherewhen the compressive strength of the MK-AL hardened paste dropsdropped to half of that under natural curing. This indicatesindicated that while the accelerated carbonation process promotespromoted strength improvementdevelopment in pure AL hardened paste, the carbonation reaction preferentially consumesconsumed CH, thereby inhibiting the pozzolanic reaction, thereby and limiting further strength development in MK-AL systems. Simultaneously, the alternating effecteffects of pozzolanic and carbonation reactions also impactsimpacted the pore structure. Under NC, the increase in MK content reducesreduced the intensity of the Ca(OH)2 diffraction peak, indicating that the pozzolanic reaction consumesconsumed part of the Ca(OH)2 and generatesgenerated products that enhanceenhanced material strength. Under AC, with the action of CO2, Ca(OH)2 iswas converted into CaCO3, suppressing the formation of pozzolanic reaction products, which resultsresulted in changes to the pore structure. In terms of porosity, all samples showed a general decrease in porosity under AC conditions, especially in MK30AL, where porosity decreased from 46.06% to 36.61%, total pore volume decreased from 0.4245 mL/g to 0.3185 mL/g, and the average pore size increased by about 42.5%. These changes indicateindicated that carbonation not only fillsfilled or transformstransformed small pores but also causescaused larger pores to dominate, leading to a redistribution of the pore structure.

4. Conclusions

Under AC conditions, pure AL hardened paste shows rapid compressive strength growth, while MK-AL systems initially increase before decreasing, with the 28-day strength halving compared to natural curing.

The carbonation accelerates the conversion of Ca(OH)2 to CaCO3, inhibiting pozzolanic reactions, particularly at 3 days, where Strätlingite's characteristic diffraction peak is absent. Additionally, AL's porosity drops from 46.06% to 36.61%, with reduced total pore volume and increased average pore size, while the pore structure redistributes, especially in systems with higher MK content.

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Lime, Metakaolin, and Graphite Pastes for Structural Monitoring

1. Introdution

Historic constructions, such as castles, cathedrals, bridges, and other ancient architectural landmarks, are valuable records of the culture and technical knowledge of past civilizations. However, preserving these structures poses a significant challenge, as they were built using traditional materials and period-specific techniques and are subject to natural deterioration over the centuries. To meet the growing demand for structural monitoring, it is essential to adopt innovative solutions that combine high mechanical strength with the ability to detect deformations in real time. A promising method involves adding piezoresistive materials to mortars, allowing continuous measurement of structural stresses and displacements.

2. Experimental Program

The first stage of the methodology involves the physical, chemical, and mineralogical characterization of the materials, followed by determining the composition of the paste mixtures for fresh and hardened state characterization tests.

2.1 Materials

Pastes containing lime and metakaolin were produced, with the addition of different proportions of graphite powder: 0%, 1%, 5%, and 10% by binder weight, as indicated by data found in the literature. This resulted in four different compositions. Physical characterization was performed through specific mass, unit mass, and laser granulometry tests. The chemical composition analysis was carried out using X-ray fluorescence spectrometry, while mineralogical characteristics were determined through X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2.2 Methods

For this study, 15 cubic specimens (5x5x5 cm) were molded based on the formulated pastes. The graphite powder addition ratios followed a previous study[1], set at 0%, 1%, 5%, and 10%. The lime and metakaolin percentages were 80% and 20%, respectively.

For all mixtures, the water-to-binder ratio was maintained at 1.0. Before preparing the pastes, the dry powders were manually mixed for 2 minutes, following the procedure from a previous study[2].

For the fresh-state assessment, the mini-slump test was conducted, measuring spread, slump, and thickness.

For electrical resistivity tests, LabVIEW was integrated with a high-precision HP 3458A multimeter. Copper plates were placed inside the specimens to allow electrical resistance measurements using the four-wire method.

1 Drougkas et al. 2023.
2 Sergio Filho et al. 2020.

The density and electrical resistance of the samples were measured every 7 days up to 49 days, allowing sufficient hardening of the mortar through pozzolanic reactions and carbonation. The density and electrical resistance were measured in three specimens per mixture. The curing process was divided into two stages: wet curing for the first 7 days, followed by air curing until the samples reached 49 days, in line with studies[1,3].

3. Results and Discussion

Fresh-state tests indicated that the addition of graphite powder, even at high concentrations (up to 10% by binder weight), did not significantly compromise the workability of the pastes. The spread values varied slightly between the compositions, with a slight decreasing trend as the graphite content increased. This behavior can be associated with the increased specific surface area of the graphite particles, which demands a higher amount of water to maintain the same fluidity; however, in this study, it was compensated by the constant water-to-binder ratio maintained at 1.0. Regarding density, all compositions exhibited a sharp reduction during the first 21 days of curing, followed by a gradual stabilization up to 49 days. This behavior is mainly associated with the evaporation of free water and the progressive occurrence of lime hydration and carbonation reactions, as also observed in similar studies[4]. The final density of the samples was lower than the values expected for traditional mortars, which can be justified by the high water content used (w/b = 1.0), the porous nature of lime and metakaolin, as well as the inclusion of graphite powder, which has a low density.

With respect to electrical resistivity, a significant increase was observed during the first 21 days, indicating the formation of a conductive network associated with the presence of graphite and, simultaneously, the reduction in moisture content, which affects ionic conductivity4. From 21 days onwards, resistivity variation occurred more gradually, suggesting that the predominant physicochemical mechanisms became the consolidation of the microstructure and the stabilization of the system through carbonation.

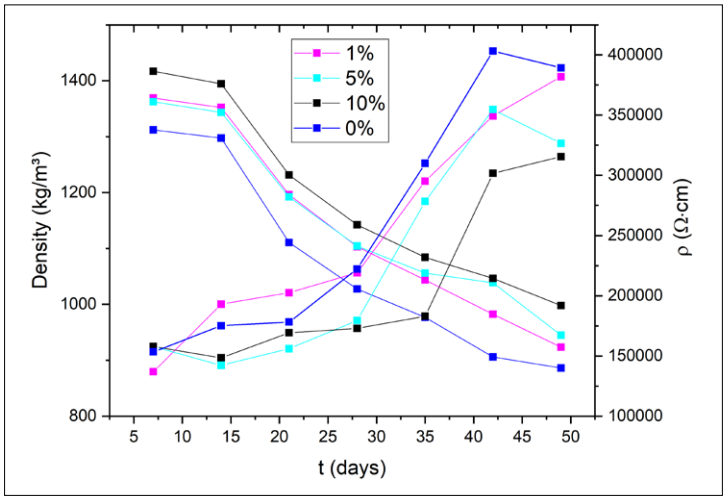

Figure 1. Gráfico da densidade e resistividade versus tempo

4. Conclusions

Graphite powder, even at 10% by binder weight, had minimal impact on paste workability, with only a slight decrease in spread values. All mixes showed a sharp density drop in the first 21 days due to water loss and ongoing hydration and carbonation, stabilizing by day 49. Electrical resistivity increased signif-

3 Azeredo 2012.
4 Zhang et al. 2023.

icantly up to 21 days, then more gradually, reflecting microstructural consolidation. The mix with 10% graphite showed the lowest resistivity, indicating enhanced piezoresistive behavior suitable for structural monitoring.

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Fluorescent Nano-Bassanite for the Consolidation of Gypsum Plasters

1. Introduction and aims

Gypsum, along with lime, has been used since the Neolithic period (12,000 - 2,000 B.C.) and played a pivotal role in the evolution of architecture across the subsequent civilizations — such as Ancient Egypt (3100–30 B.C.), Greek (800–146 B.C.), and Roman (753 B.C.–476 A.D.) — until present times, remaining one of the most demanded binders in the world, especially for its application in the construction industry. Despite gypsum's historical relevance and widespread traditional use, it still presents several challenges, such as reduced mechanical strength in wet conditions or relatively high solubility compared to other traditional binders. Also, gypsum becomes unstable at temperatures above ~42 °C[1]. In such conditions it can undergo dehydration to form bassanite or anhydrite, transitions that imply a significant reduction in molar volume, triggering mechanical stresses typically manifesting in the form of cracks, spalling and, in more serious cases, partial or total disintegration of the original structure. Additionally, prolonged exposure to high relative humidity values and extreme temperature fluctuations — conditions that are expected to aggravate due to climate change — has been identified as a major cause of damage to gypsum plasterworks[2-3-4] and has been linked to increased porosity and reduced surface hardness[5]. These pathologies have been observed in the case of historical gypsum plasters in monumental sites of recognized cultural importance, such as the Alhambra, in Granada (Figure 1a). The impact of these deterioration agents has been investigated through field observations and laboratory studies, including accelerated aging protocols. However, it is critical to further develop durability testing methodologies that provide transferable results to inform in a more realistic manner on current or anticipated challenging exposure conditions, considering climatic regions where gypsum plasters are part of local construction history and traditions as well as long-term predicted major environmental shifts due to climate change[6].

Moreover, while extensive conservation methods and materials are available to address similar pathologies in other building materials, such as lime mortars and stone, there is a need to expand treatment options specifically tackling the deterioration of gypsum-based materials. In this respect, the use of consolidants may become useful. Conventional requirements for consolidants include improving surface cohesion and prevent further deterioration of treated substrates, while not inducing a significant mismatch in terms of the physical, chemical, and mechanical properties, and not affecting the original appearance but at the same time enabling to identify treated areas. However, consolidation products currently used in conservation interventions on gypsum plasterworks are the same as those applied to lime mortars or stone materials (e.g., acrylic and vinyl resins, alkoxysilanes, and nanolimes), whose efficacy and potential incompatibility issues need further investigation[7].

1 Mishra et al., 2025.
2 Cotrim et al. 2008.
3 Caroselli et al. 2019.
4 Freire et al. 2019.
5 Blasco-Lopez et al. 2013.
6 Sabbioni, Brimblecombe and Cassar 2010.
7 Ramamurthi et al. 2022.

From a conservation point of view, in this work we exploited the versatility of bio-inspired crystallization processes for the synthesis of fluorescent nano-structured bassanite, which we employed as a highly compatible consolidant for the preservation of weathered gypsum plasters when applied as an alcoholic dispersion (Figure 1b)[8]. We investigated the occlusion of calcein during the gypsum crystallization to study its impact on crystal morphology from an integrated fundamental and applied research perspective. To do so, we analyzed variations in chemical and crystallographic properties by using high-resolution X-ray diffraction (HR-XRD), Fourier-transformed infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), and scanning transmission electron microscopy (STEM). One major result is that gypsum formed upon the hydration of the chemically and structurally modified nano-bassanite shows greater resistance to dissolution when fluorescent calcein is occluded between gypsum crystal domains. Furthermore, fluorescence provides additional advantages in treatment assessment, allowing the precise identification of treated areas and penetration depth as well as distribution within the substrate, without altering the appearance of the treated substrate because the treated areas are only evidenced upon illumination with UV light (Figure 1c). Importantly, preliminary nano-indentation results have demonstrated an increase in physical damage tolerance in gypsum crystals modified with calcein.. Ongoing research is developing accelerated aging protocols to better inform on the response of gypsum plasters to realistic stressful environmental conditions, whether current or anticipated according to accepted climate change models. The outcome of this research will be contributing to the practical conservation of gypsum plasters with effective treatments options and protocols for testing their durability.

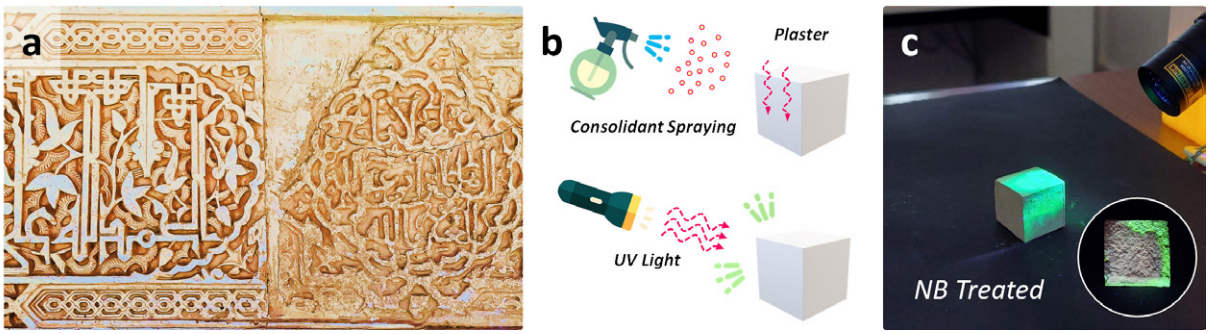

Figure 1. a) Typical surface deterioration patterns observed in historical gypsum plasters from the Alhambra (Granada). b, c) Simple methodologies applied for consolidation treatments and detection through UV illumination

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The search for new formulatons in consolidation: the use of nanolime for the consolidation of mortar preparation of the Colosseum southern ambulatories and the pedestal of the Trajan Column

1. Introduction

The Parco archeologico del Colosseo carries out conservation activities on the heritage in its care by pursuing a policy of environmental sustainability and compatibility of intervention materials along with the search for conservation means not harmful to operators and environment.

These instances have converged in 2021 in the "PArCo Green", a project born to reduce the environmental impact of PArCo's activities; on this track the Memorandum of Understanding with the University of L'Aquila, Department of Industrial and Information Engineering and Economics was signed, focusing on the experimentation of calcium hydroxide nanoparticles (nanolimes) in aqueous suspension, obtained through an innovative and sustainable process, for the consolidation of carbonatic matrix materials in order to research consolidation practices aimed at preserving the chemical-physical and mineralogical characteristics of the original substrates, without altering its features while respecting the environment.

We would like to present, on this occasion, some of the conservation activities carried out in the last two years (2022-2024): the first case is the consolidation of mortar surfaces unearthed in the archaeological excavation of the outer ambulatories of the southern portion of the Colosseum. This is a putty lime-based floor preparation, setting bed of the original travertine floor blocks that were later removed. In the same occasion the roman concrete belonging to the foundation ring of the building as well as thr pozzolanic matrix mortar belonging to the floor construction system were consolidated. These mortar substrates marked by different composition and conditions, had in common a major surface decohesion. The decision to keep them visible in the subsequent arrangement of the square of the Colosseum led to the need to formulate a consolidation method specifically designed for these materials

The use of nano-lime in aqueous suspension was also chosen for restoring the cohesion of the surfaces of the Luni (Carrara) marble base of the Trajan Column. The restoration of two sides of the plinth, southwest and northwest, was carried out in 2024; the surfaces of the Trajan Column are marked by a significant decohesion phenomenon, due to prolonged exposure and weathering, fine surface carving, and the natural feature of the stone, which led to a progressive partial loss of the cortical layer. The reestablishment of the cohesion of these surfaces has presented several issues; these were related to the presence of metal oxides as a the natural content of the Luni marble, which has oxidized due to prolonged weathering, and the prolonged percolation of metal oxides from the summit bronze statue conveyed by rainwater.

The desire not to alter the original materials by applying products of a different nature and mechanical properties from the original led, once again, to opt for this method of consolidation. In the course of the applications, it was necessary to investigate the possible interactions between the nanolime and the different metal oxides present on the stone.

Both interventions were supported by a thorough diagnostic phase; held in situ and in the laboratory, aimed at ascertaining the state of conservation of the constituent material, its petrographic and mineralogical characteristics and the effectiveness of the treatments.

1.2 The nanolimes in water and the in- situ treatments on the archaeological excavation of the Southern front of the Colosseum and on the Colonna Traiana

In the preservation of carbonatic-matrix surfaces, the use of calcium hydroxide nanoparticle suspensions (nanolimes) may be very promising because of their potential peculiarities to restore mechanical strength and surface cohesion while preserving the chemical-physical and mineralogical characteristics of the original substrates, without inducing the formation of compounds that may alter the inherent properties of the treated substrates. The consolidating action and compatibility of nanolimes are closely related to the completeness of the carbonation process, which can create new nano-micro crystals of calcium carbonate in the treated substrate. Precisely because of the possibility of complete carbonation, the size of the nanoparticles but also the presence of water are the two fundamental factors behind the consolidating action of nanolimes, especially in extensive or in situ applications.

At the University of L'Aquila (UNIVAQ), an original and sustainable synthesis has been developed to obtain a new, uniquely water-dispersed nanolimes, based on a single-step, ion-exchange process that operates in water, at room temperature and ambient pressure, in a short time procedure, with low energy consumption and no toxic or polluting effluents (European patent EP 2880101B1. 2016). Thanks to the innovative process technology of the UNIVAQ spin-off, SNAPTECH SRL, nanolime in water are now obtained on a large scale to be able to enable extensive treatments for the consolidation of historical surfaces with a carbonate matrix, respecting the original materials and the environment.

To define the application protocol of nanolime, a study of the original materials was first carried out by mineralogical-petrographic surveys, X-ray diffractometry, porosimetry, and FESEM-EDS electron microscopy. Due to the results obtained, ad hoc nanolimes, NANOLAQ COLOSSEO, were also defined, and the compatibility and effectiveness of the treatments carried out was first checked in the laboratory on representative samples by petrographic analysis, FESEM-EDS, porosimetry, tearing tests (Scotch Tape Test, STT), and microdrilling tests (Drilling Resistance Measurements System, DRMS). The study of substrates and preliminary treatment tests in the laboratory, carried out to identify the best solutions regarding the choice of consolidant and method of application, were fundamental in establishing an intervention protocol to be transferred in situ. In the final stage of the work, in fact, the nanolimes were applied in situ and the consolidating effectiveness of the treatments was analyzed by STT and DRMS.

The results showed that the choice of an ancient and, at the same time, innovative material such as nanolime, used in synergy with water, was able to define a treatment that did not change the chemical and physical features of the original materials, showing an effectiveness in consolidating both the pozzolana and the setting bed mortar of 66% and 85%, respectively, with an increase in mechanical strength both near the surface and up to 2 cm deep (Figure 1).

As for the consolidation of the marble of Trajan's Column, again NANOLAQ nanolime showed a good ability to restore surface cohesion without altering the characteristics of the original substrate or interfering with any contamination due to interactions with the surrounding environment; in this case the nanolime was also used as a surface protection layer.

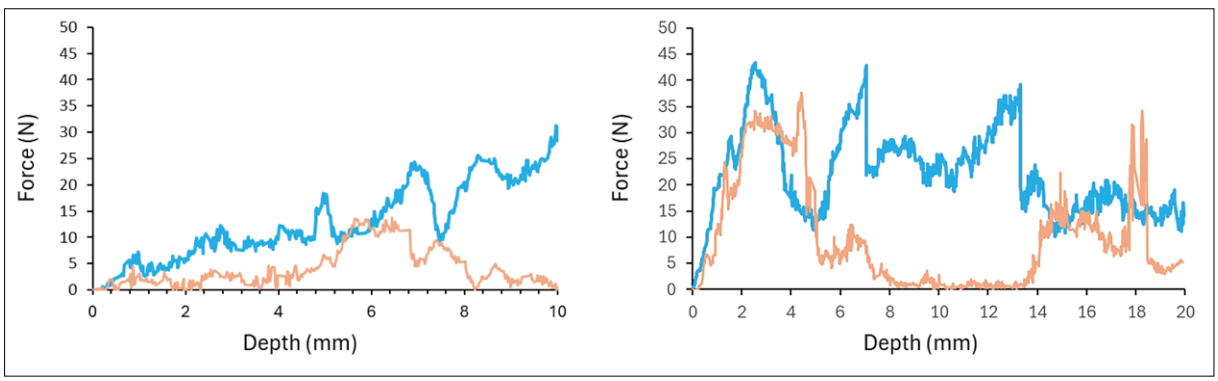

Figure 1a-b. DRMS measurements carried out on setting bed mortar: (a) laboratory tests; (b) in situ tests. Legend: average values of untreated surface: orange curve; average values of NANOLAQ treated surface, blue curve

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Barium-Phosphate Treatment for Salt-Contaminated Heritage Materials: Enhancing Durability and Sustainability in Restoration

1. Introduction

This study investigates the development and application of barium-phosphate treatments to enhance the properties of building materials contaminated with soluble salts, particularly for restoration efforts on carbonate-based substrates, such as mortars, plasters and renders. The main goal is to evaluate the effectiveness of barium-phosphate solutions as an innovative alternative to conventional techniques, focusing on minimizing byproducts, improving reaction efficiency, and reducing potential hazards to both operators and the environment, while maintaining the integrity of the treated material[1]. The treatment aims to enhance material properties without altering moisture transport behavior or introducing internal tensions between the grains. Specifically, the research uses barium-phosphate solutions to convert soluble sulfates into insoluble phases such as barium sulfate (BaSO4) and calcium phosphates. Additionally, another chemical reaction is expected to improve the durability and stability of the material by forming apatite-like phases[2], which can incorporate sulfate and barium ions into their crystalline structure. The use of green solvents and components that minimize byproduct formation is emphasized to further enhance reaction efficiency and reduce environmental impact.

2. Experimental

2.1 Materials

The tests were conducted on prismatic test specimens, which were prepared using metal moulds[3]. The specimens measured 40 mm x 40 mm x 40 mm and were made from a slaked lime and sand mixture in a mass ratio of 1:8, with medium-grained sand (0-2 mm) being used. Before the treatment, the specimens were soaked for 2 hours in a 0.3 mol/l MgSO4 solution. The barium-phosphate treatment was then applied after the specimens had lost approximately 90 wt.% of their water content. They were stored in a controlled humid environment with a relative humidity of 70-75% and a temperature of 20-22 °C until they reached a constant weight. Following the treatment, some of the samples were ground in a mortar, stirred in deionized water for 4 hours, and then slow filtered. The soluble fraction was separated from the insoluble fraction by weighing the filter cakes. The filtrate was prepared for chemical analysis with ICP-EOS. Other samples were subjected to mechanical stress tests.

2.2 Results

The experimental results demonstrated that the barium-phosphate treatment successfully converted sulfate ions into insoluble compounds. Table 1 shows that after just one application, approximately 50 wt.% of the sulfate ions were fixed into insoluble phases. Scanning Electron Microscopy (SEM) and Energy Dis-

1 Rong et. al. 2022.
2 Nikolenko et. al. 2020.
3 DIN EN 1015-11 - Annex A.

persive X-ray Spectroscopy (EDX) analyses revealed that after the second application of the barium-phosphate solution, the coating formed was more homogeneous and evenly distributed across the carbonate matrix and sand grains. The phases formed were primarily substituted apatite (calcium, barium, and magnesium phosphate phases), with high crystallinity and a Ca/P molar ratio of approximately 1.67 (Figure 1). These findings indicate that the high pH and adequate supply of calcium and phosphate ions in the solution promote the formation of calcium phosphate phases, contributing to enhance physical-mechanical properties of the treated material without causing noticeable color changes. A color difference ΔE^* of 1.6 ± 0.6 after two applications of the treatment, which is barely noticeable to the human eye. Compressive strength tests on treated samples showed a marked improvement in mechanical properties, even after just one week of treatment, indicating early consolidation of the material. In addition to sulfate fixation, the barium-phosphate treatment significantly improved the mechanical properties of the material. The compressive strength of the treated samples increased substantially, with a significant enhancement even after just one week of treatment. Values of 0.4 ± 0.04 N/mm2 (value ± standard deviation, n=3) were measured in comparison to the untreated material with a compressive strength of 0.2 ± 0.04 N/mm2. This suggests that the barium phosphate treatment facilitates material consolidation and strengthens the substrate, making it more resistant to physical stresses.

Theoretical ion content after:	Ca2+ wt%	Ba2+ wt%	Mg2+ wt%	SO42- wt%	PO43- wt%	pH	LF [mS/cm]
1 barium-phosphate treatment		0,3	0,2	0,9	0,6	-	-
2 barium-phosphate treatments		0,5			1,1		
Ion content after samples elution:							
1 barium-phosphate treatment	0,1	0	0,05	0,5	0	8,8	2,9
2 barium-phosphate treatments	0,1	0	0,02	0,4	0	9,1	2,5

Table 1. Theoretical ion content calculated from the absorbed solutions and results of the quantitative chemical analysis on analytes after stirring the samples in deionized water.

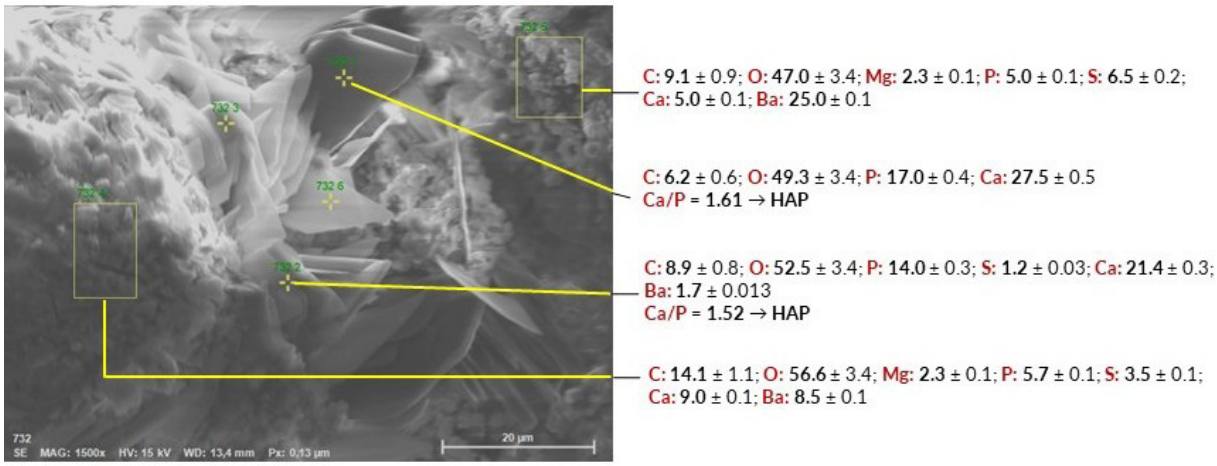

Figure 1. SEM images and EDX elemental analysis in a sample after two treatments with barium-phosphate solution. The results are given in atomic percentage (at % ± 1σ)

3. Conclusion and Outlook

The findings of this study indicate that barium-phosphate treatments offer a promising solution for materials contaminated by soluble salts, performing dual functions of sulfate fixation and material consolidation. The treatment enhances the mechanical properties of the material and stabilizes the structure

without introducing byproducts. This approach holds promise for the long-term preservation of heritage materials, particularly those vulnerable to sulfate-induced deterioration. Future research should focus on refining the treatment process and examining the long-term effects on material properties to ensure its sustainability and effectiveness as a conservation method.

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ANTONIA TIGRANO, GERALD ZIEGENBALG

Consolidation of Gypsum-Containing Substrates with Newly Developed Nano-Gypsum Dispersions

1. Introduction

Plasters and renders are vital materials in building construction, particularly in the context of historical structures[1-2]. They are used for aesthetic finishes, insulation and protection, making them crucial for a building's longevity. However, these materials can be vulnerable to environmental degradation, including cracking, erosion, and moisture damage. Various surface treatments have been explored to improve the durability of gypsum-based materials . The use of gypsum-based nanomaterials, with their enhanced surface area and chemical reactivity, present a promising alternative. This study investigates a newly developed nano-gypsum dispersion designed to improve the mechanical stability and longevity of gypsum-based materials[3]. The research explores specific methods of application by controlled dripping until saturation and post-treating techniques to optimize the consolidation performances. By exploring this innovative product and approach, the findings of this research could lead to more environmentally friendly construction practices and offer valuable insights for enhancing the longevity of plaster and render materials in both contemporary and historic contexts.

2. Nano-gypsum dispersions properties

The nano-gypsum dispersions developed at IBZ-Salzchemie consist of solid calcium sulphate particles dispersed in ethanol/water mixture. These dispersions range in size from 100 nm to 4 µm (d50 = 250 nm) and contain hemihydrate ($CaSO_4 \cdot ½H_2O$) and dihydrate ($CaSO_4 \cdot 2H_2O$) phases (Figure 1a). The nano-gypsum dispersion is versatile and can be mixed with various solvents such as ethanol, iso-propanol, or n-propanol in any desired ratio. This flexibility allows for tailoring the dispersion to specific requirements or preferences based on the desired application method or surface characteristics. They can be applied via spraying onto the surface, with a pipette, with injections, and with manual or pressured spraying/nebulizing systems. The nano-sized gypsum dispersions are harmless to the material to be treated. As the ethanol evaporates, the gypsum dihydrate crystals are deposited in the pore space of the material and are stabilized by the setting of the hemihydrate component. A post-treatment with deionized water improves penetration depth (Figure 1b) and ensures a complete phase transformation of the hemihydrate to dihydrate with minimal expansion or crystallization pressure.

3. Material and methods

Test specimens (mortar prisms 40 x 40 x 40 mm^3) with different aggregate/binder ratio, structure and density were prepared and divided in groups:

1 Silveira et al. 2007.
2 Elsen 2006.
3 Jroundi et al. 2014.

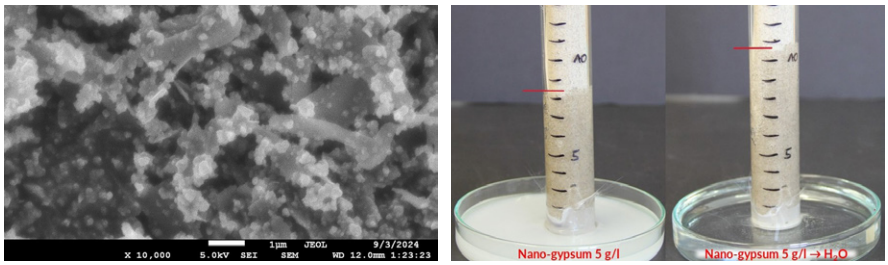

Figure 1. (a) Left: SEM image showing the solid particles that constitute the nano-gypsum dispersions. (b) Right: Comparison of capillary rise between the nano-gypsum dispersion in a sand-filled tube (8.5 cm) and the same tube placed in water (11.5 cm)

a) Highly porous gypsum mortars: 70 wt.% medium-grain sand (up to 2 mm), 30 wt.% gypsum β-hemihydrate (Keramod 125, CASEA).
b) Low-porous gypsum mortars: 70 wt.% medium-grain sand (up to 2 mm), 30 wt.% gypsum β-hemihydrate.
c) Dense gypsum mortars: 50 wt.% medium-grain sand (up to 2 mm), 50 wt.% gypsum β-hemihydrate.
d) Medium porous lime/gypsum mortars: 80 wt.% medium-grain sand (up to 2 mm), 20 wt.% binder composed from gypsum β-hemihydrate 70 wt.% and slaked lime 30 wt.% (IBZ-Salzchemie).
The nano-gypsum dispersions were applied by controlled dripping until saturation, followed by a light deionized water spray to enhance penetration. To prevent rapid ethanol evaporation and back-transportation of solid particles, specimens were covered with foil and stored until weight constancy was reached. Microscopic surface analysis and mechanical testing (including compressive strength and adhesion tests) were conducted to evaluate the effectiveness of the treatment.

4. Results

Nano-gypsum dispersions demonstrated effective penetration and consolidation of gypsum-based materials without altering their visual appearance. The results for each group of test specimen are shown in table 1. The nano-gypsum dispersions were able to penetrate deeply into the treated porous material. The denser samples of the group b and c were treated with two less concentrated nano gypsum dispersions and also were able to penetrate effectively, reaching a significant depth. After treatment of the highly porous mortar, no significant changes in appearance were observed. The same applies to the low-porosity and dense mortar prisms. Microscopic analysis revealed a homogeneous distribution of gypsum particles within the pore space. Adhesion tests showed a significant reduction in detached surface particles after treatment, as described in table 1, confirming improved material cohesion. Additionally, compressive strength tests on lime/gypsum mortars indicated a notable increase in mechanical stability, rising from 2.0 ± 0.4 N/mm² to 3.4 ± 0.6 N/mm² (value ± standard deviation, n = 3).

5. Conclusion and outlook

This study highlights the potential of nano-gypsum dispersions as an effective surface treatment for gypsum-based materials. The dispersions improve mechanical stability and adhesion while ensuring deep penetration into various substrate types. These findings suggest significant benefits for both historical

Test group	Concentration [g/L]	Penetration depth (with post-treatment)	Peeled-off material untreated [mg]	Peeled-off material treated [mg]
a	5	trough	26	15
b	4	18 mm	49	7
c	3	12 mm	14	5
d	5	trough	-	-

Table 1. Results data of the conducted analysis on the test specimens before and after treatment with nano gypsum dispersions (value ± standard deviation, n = 2)

restoration and modern construction, reducing material degradation and prolonging structural integrity. Future research will explore long-term durability under different environmental conditions and optimize formulation for large-scale applications.

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CRISTINA DE NARDI, GERALD ZIEGENBALG

Advancing Heritage Conservation: Evaluating Healing Agents for Mimetic Self-Healing Technologiesevaluating an innovative nanolime dispersion in 3D printed vascular self-healing systems

1. Introduction

Climate change is subjecting our built heritage to increasingly severe hazards, highlighting the need for innovative masonry repair technologies to ensure long-term resilience. A range of traditional intervention strategies, such as repointing and bed joint reinforcement, are available to repair damage in masonry structures[1]. However, these methods have a limited lifespan and are often ineffective[2]. There is a growing interest in self-healing technologies for historic masonry, driven by the need to preserve heritage structures while maintaining their original materials and aesthetics. Incorporating self-healing properties helps minimise frequent repairs, reducing maintenance costs and ensuring the long-term stability of historic buildings. In this context, researchers are investigating different strategies, including bio-based healing agents[3], mini vascular networks in mortar[4], and autonomous crack repair mechanisms[5]. Choosing the right healing agent is essential for a vascular system's success. It must be stable over time, trigger self-healing moratrs, have low viscosity for efficient flow and crack penetration, be compatible with historic materials, and be non-toxic for environmental and construction safety. Nanolime, a dispersion of calcium hydroxide nanoparticles in alcohols, is widely used for consolidating historic masonry and modifying mortars or grouts[6]. Its small particle size allows deep penetration, but challenges such as rapid alcohol evaporation and formation of metastable carbonates require careful post-treatment. To enhance its effectiveness, nanolime can be combined with silicic acid esters (SAE)[7]. This combination improves surface consolidation by forming an adhesive bridge between calcium hydroxide and silica gel while also accelerating SAE hydrolysis.

This study evaluates the potential of an innovative nanolime dispersion, termed Adv-NL, created by combining the commercial product CaLoSiL® with SAE for use as a healing agent. Specifically, it aims to assess its suitability for encapsulation while meeting key requirements for self-healing technologies in built heritage contex: (i) long-term stability in liquid form, (ii) chemical compatibility with carriers to prevent alterations in their mechanical properties.

2. Materials and methods

Longevity tests were performed on tubular capsules (inner diameter = 4 mm, length 40 mm, double wall thickness 0.25 × 2 mm) printed from clear Polylactic acid (PLA) filament (2.75 mm in diameter) purchased from Verbatim®, using an Ultimaker2+® printer with a 0.25 mm nozzle. The tubular capsule design and the main printing parameters are reported in Figure 1.

1 Valluzzi et al. 2005.
2 Harding P. 2023.
3 Vučetić et al. 2023.
4 De Nardi et al. 2024.
5 De Nardi et al. 2017.
6 Rodriguez-Navarro et al. 2018.
7 Ziegenbal 2024.

Printing parameters	
nozzle	0.25 mm
layer height	0.06 mm
support type	buildplate
bottom_layers	8
cool_fan_speed	80
infill_sparse_density	100
support_infill_rate	2
support_z_distance	0.25
top_bottom_pattern	grid
top_bottom_thickness	0.06 mm
top_layers	5
wall_line_count	16
wall_thickness	0.25 mm
xy_offset	0

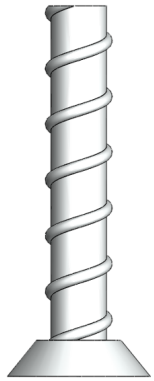

Figure 1. Design of tubular capsules and corresponding printing parameters.

Capsules were filled with approximately 0.7 mL of advanced nanolime dispersion (Adv-NL) provided by IBZ-Salzchemie GmbH & Co. KG (Germany), sealed with silicone, and broken at 7, 14, 21, and 28-day intervals to evaluate the physical condition of both the healing agent and the PLA polymer. Capsules were stored in laboratory condition (20° ± 5, RH ~ 45 %). Over 4 weeks, 12 were tested, with 3 opened at each interval.

3. Results

The results of the Adv-NL longevity tests are summarised in Table 1. It is important to note that changes in both the viscosity of the healing agents and the PLA polymer were assessed through visual inspection, providing only a qualitative approximation of any variations. The letters L, G, and S indicate the following states: Liquid (L) – no noticeable change, Gel (G) – beginning to exhibit solid-like behavior, and Solid (S) – fully solidified. The polymer's consistency was evaluated by breaking the capsules and observing the fracture behavior: Brittle (B) indicated a brittle rupture, while Ductile (D) suggested a more flexible failure, which was considered a sign of early polymer degradation.

From the results, it can be seen that the Adv-NL solution remained liquid throughout the 28-day period, without any noticeable change in viscosity. No significant alterations in the PLA polymer were observed, as it consistently exhibited brittle fracture behavior. However, a decrease in volume was detected (~10%), suggesting a possible partial absorption of the Adv-NL into the polymer matrix or gradual evaporation over time. This could indicate minor interactions between the healing agent and the encapsulation material, which may warrant further investigation to ensure long-term stability.

Clear PLA capsules	Test duration (days)			
	7	14	21	28
Adv-NL	I/B	I/B	I/B	I/B

Tabel 1. Longevity test of Adv-NL in clear PLA.

4. Conclusion

From the analysis of the results presented in this paper, the following main conclusions can be drawn:

-Advanced nanolime, combined with silicic acid esters (Adv-NL), demonstrates strong potential as a healing agent for self-healing technologies that rely on encapsulation, including vascular and mini-vascular networks.

-Adv-NL meets the essential criteria for these technologies, including maintaining low viscosity over time when encapsulated in PLA polymer capsules, without inducing any significant changes in the polymer. A slight volume reduction has been observed, suggesting partial evaporation/absorption.

Acknowledgments
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ANTY SINCIA ALOYSINO, ENRICO SASSONI

Consolidation of wall paintings by diammonium hydrogen phosphate (DAP)

1. Introduction

Diammonium hydrogen phosphate (DAP) was proposed in 2011 for consolidation of carbonate substrates . The idea is reacting the substrate with an aqueous solution of DAP, so that calcium ions from the substrate and phosphate ions from the solution can form new calcium phosphates with consolidating properties1. The ideal mineral to form is hydroxyapatite (HAP, Ca10(PO6)4(OH)2), as it is the most stable calcium phosphate at pH > 4. In general, the DAP-treatment was shown to provide high mechanical consolidation, without significantly altering the color of the treated substrate and its transport properties[1], which allows for good durability of the treated substrate.

After the first promising results obtained on stone, the DAP-based treatment has later been explored also for conservation of lime-based mortars[2-3]. In view of possibly using DAP solution for the conservation of wall paintings, the effects of DAP solutions onto pigments (tested alone, as powders) have also been explored[4]. In the light of the good results obtained on lime-based mortars and pigments, in the present study for the first time the DAP-based treatment was tested on fragments of real wall paintings, coming from 8 churches in northern Italy.

2. Materials and Methods

2.1 Samples

Samples used for the tests were fragments of real wall paintings, already detached from the substrate and no longer re-attachable, comprising examples of fresco and secco techniques and dating from the IX to the XV century.

2.2 Consolidating treatment

The samples were treated with an aqueous solution containing 1 M DAP+1 mM CaCl2, applied by poultice prepared using cellulose pulp (1:4 w/w ratio between the cellulose pulp and the solution). After the poultice application, the samples were wrapped with a plastic film, to prevent evaporation. After 24 h, they were unwrapped, rinsed with water and dried at 40 °C until constant weight.

2.3 Characterization

The sample morphology, before and after treatment, was observed by scanning electron microscopy (SEM), by using a Tescan Mira3 FEG-SEM, equipped with EDS analysis. The mineralogical composition of

1 Sassoni, Naidu, Scherer 2011.
2 Balonis, Ma, Kakoulli 2013.
3 Sassoni, Franzoni 2020.
4 Ma, Pasco, Balonis, Kakoulli 2019.

the samples was analysed before and after treatment by X-ray diffraction, by using a PANalytical X'Pert PRO diffractometer.
The consolidating effectiveness of the DAP-based treatment was determined by scotch tape test, by comparing the material loss registered on the same sample before and after consolidation.
The treatment compatibility was assessed by visual observation and by measuring the CIE Lab colour parameters on the same sample, before and after treatment.
The durability of the treated samples was evaluated by subjecting them to an accelerated ageing test, consisting in repeated freezing-thawing cycles, whose effects were evaluated by visual observation and material loss.

3. Results and Discussion

After treatment with the DAP solution, newly formed carbonate HAP (Ca10(PO4)3(CO3)3(OH)2) was detected in the samples. Because many samples initially contained dolomite (which can be ascribed to the use of magnesian limes for the plasters preparation), in many cases also struvite (NH4MgPO4•6H2O) was evidenced by XRD and SEM-EDS.
Thanks to the formation of these new phases, a significant reduction in material loss by scotch tape test was registered in all the samples (Figure 1).
In terms of chromatic compatibility (Figure 1), only in 7 samples out of 30 a colour change $\Delta E^*>5$ was registered. Notably, in all the samples that exhibited a colour change higher than the commonly accepted threshold of $\Delta E^*=5$ struvite was detected, but many other samples where struvite was formed exhibited minimal colour change, hence struvite formation seems not to be the decisive factor.

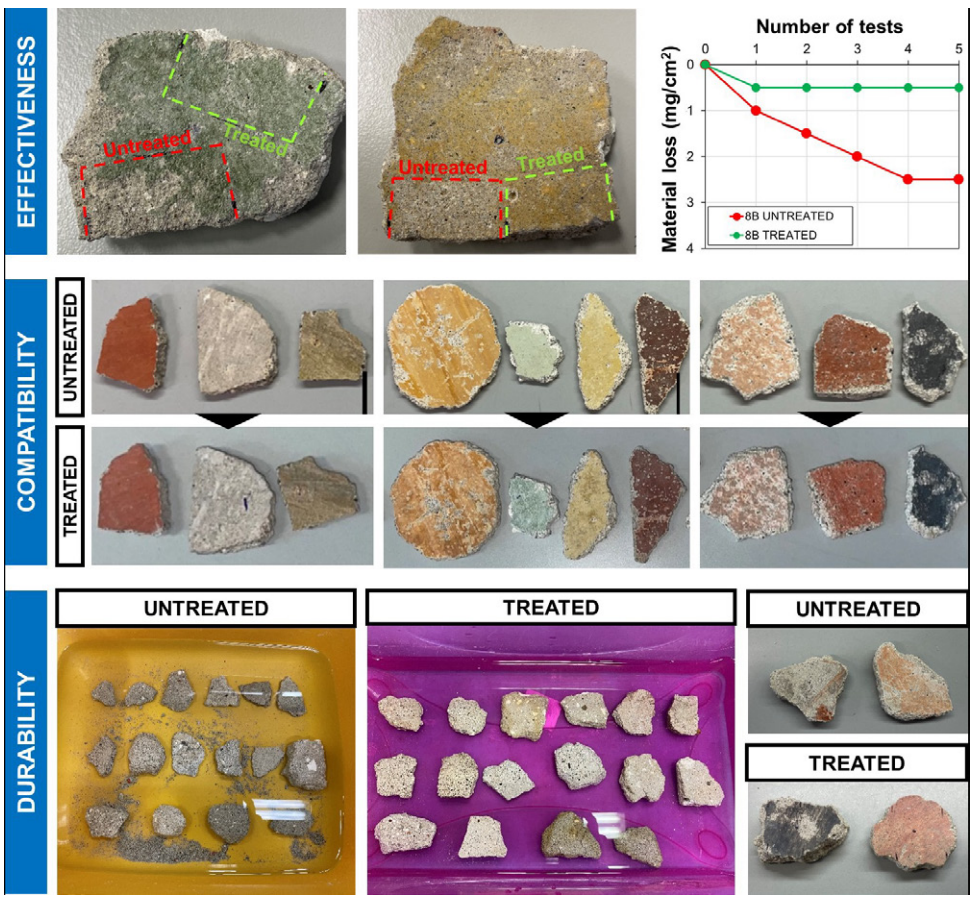

Figure 1. Examples of the effects of the consolidating treatment in terms of effectiveness, compatibility and durability.

When the samples were subjected to accelerated ageing, consolidated samples resisted freezing-thawing cycles significantly better than the untreated references (Figure 1), thus exhibiting sensibly lower material loss.

4. Conclusions

The results of the present study, reporting for the first time the effects of the DAP-based treatment when applied onto fragments of historic wall paintings, suggest that the treatment combines promising effectiveness, chromatic compatibility and resistance to freeze-thaw cycles. Formation of struvite was systematically assessed, as a result of the presence of Mg in the substrate, but it does not appear to prevent the treatment success.

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Smart plaster in Historical Buildings

1. Introduction

Historic buildings usually give us a sense of wonder and encourage us to learn more about the people and culture that built them. Moreover, the presence of historic buildings can further utilize their functional, social, educational, and economic aspects. According to European research, inefficient buildings contribute up to 40% of the total energy consumption in the EU during their life cycle, therefore, in times of energy crisis and during transition to low-carbon society different improvements regarding the thermal efficiency of the buildings should be made. Given the large energy-inefficient building stock, the energy-efficient renovation of older buildings is one of the most important measures in the green transition. This goal is difficult to achieve for buildings that are part of our cultural heritage, thus smart materials can help us achieve this goal.

In this study, a plaster with phase change materials (PCM) is presented. Phase change materials (PCMs), which store or release energy through latent heat, have been shown to be particularly effective in reducing heating (daytime) and cooling (night-time) loads in buildings, managing peak energy demand, maintaining thermal comfort, while providing significant economic and environmental benefits.

2. Materials and properties of plaster

The samples (mortar bars) were prepared with hydrated lime (CL-90 (92% Ca(OH)2 and less than 5% MgO) and white cement CEM I 52.5R as binder. Dolomite sand of fraction 0/2 and a density of 2848 kg m-3 was used as an aggregate. The addition of PCM slurry to the mixture was 30% by volume for the samples (P). The reference samples (R) are without PCM addition. The mortar bars (40x40x160 mm) were prepared according to standard EN 1015-11. The results of the fresh and hardened properties of the mixtures are given in Table 1.

	Fresh plasters			Hardened plaster			
Sample	Ability to flow/mm	Porosity / %	Bulk density / kg m^{-3}	Bulk density / kg m^{-3}	Porosity / %	Compressive strength / MPa	Flexural strength / MPa
R	140.0	5.6	2280	2101	20.17	13	5.9
P	208.6	2.8	2150	1954	23.43	7.9	5.4

Table 1: Properties of the investigated mixtures in fresh and hardened state.

3. Microstructure and thermal properties of plaster

The microscopic analysis by SEM revealed a high degree of microstructural homogeneity, characterized by a uniform distribution of PCM microcapsules in the matrix. The microcapsules, ranging in size from 1 µm to 20 µm, are incorporated without significant aggregation or segregation, ensuring uniform performance of the entire composite material (Figure 1). Using SEM, we were able to demonstrate that the

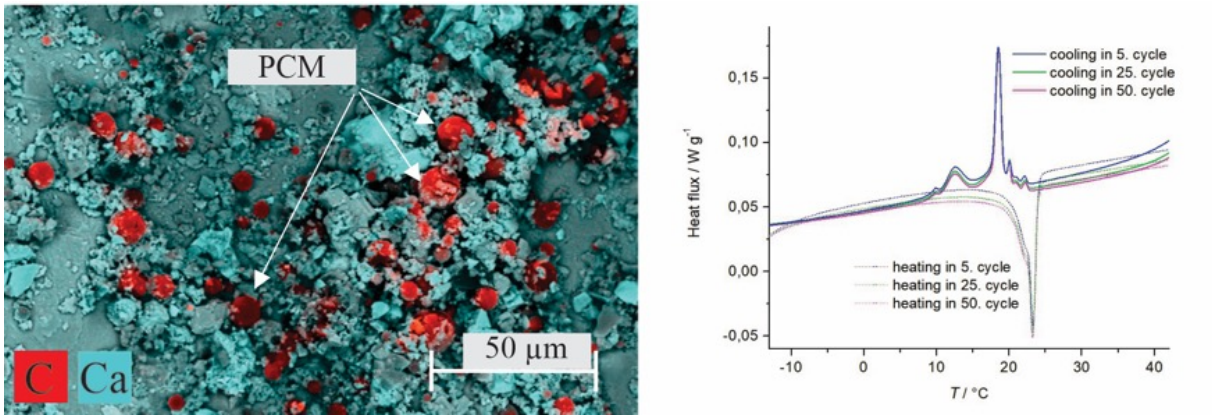

Figure 1. SEM microscopic analysed of plaster with PCM (left). DSC curves for 5th, 25th and 50th cycle of sample P (right)

encapsulated PCM capsules remained intact throughout the mixing process, indicating the mechanical resistance of the microcapsules and their ability to withstand the shear forces encountered during plaster preparation.

The results of the temperature drop measurements and differential scanning calorimetry (DSC) show a remarkable influence of the PCM content on the thermal behaviour of the composites during the cooling process. In general, the temperature drop of PCM composites (P) is slower in the temperature range corresponding to the crystallization interval of the PCM. Moreover, the PCMs showed stability at the phase change temperatures and stability of enthalpies with their minimal deviations between cycles (Figure 1).

4. Model of the thermal performance of the plaster

The study on the thermal performance of a historical building with applied PCM plaster was carried out on a model building in Velenje, positioned in Continental Climate (i.e., PCM system, Ve = 60 m3, Au = 20 m2) using PCM Express 1.0.3 software (EnergieSoftware GmbH, 2024). The PCM model is a massive stone structure, historically protected (U = 1.7 W/(m2K)) and has applied PCM 23 plaster for the finishing (15 mm). The transparent part of the envelope is an N, E, W oriented, thermally insulated double glass window with a wooden frame (Aw, total = 11 m2, Uw =1 W/(m2K)). Ventilation mode is natural. The air temperature set points are 22 °C for heating and 25 °C for cooling. The results were compared with the same building without PCM (i.e., conventional model) and other location (Koper, Mediterranean Climate) (Figure 2).

The results of the inside air temperature evaluation (Table 1) showed a higher thermal performance of the PCM model compared to the conventional model located in Velenje (Continental Climate). The PCM model improves thermal comfort, as over the observation period, the air temperature is within the thermal comfort range (21 - 26 °C) 43.7% (3828 hours) of the modelled time in case of the PCM system and 33.9% (2970 hours) of the modelled time for the conventional model, respectively. At temperatures above 26 °C, the PCM model exhibited 5.1% (447 hours) of the modelled time staying in the thermal comfort range, while conventional model stayed in thermal comfort range 12.2% (1069 hours) of the modelled time.

Similar conclusions can be made about the Koper Mediterranean climate. The air temperature within the thermal comfort range (21 - 26 °C) was maintained 37.4%

Figure 2. Location of studied models and traditional stone buildings for thermal comfort and energy efficiency analysis

(3276 hours) of the modelled time for the PCM system and 30.8% (2698 hours) of the modelled time in the conventional model. Above 26 °C, PCM model stayed 26.0% (2278 hours) within the thermal comfort range and 29.6% (2593 hours) in case of the conventional model.
The findings are comparable with other studies by[1] which confirm the valuable value of PCM towards achieving sustainability and the comfort of historically protected buildings.

Model type / Location	PCM model		Conventional model	
	Velenje	Koper	Velenje	Koper
Temperatures within comfort range (21-26°C)	43.7% (3828 h)	37.4% (3276)	33.9% (2970 h)	30.8% (2698 h)
Temperatures above comfort range (> 26°C)	5.1% (447 h)	26.0% (2278 h)	12.2% (1069 h)	29.6% (2593 h)

Table 2: Evaluation of room temperature according to the comfort range temperatures for two models (PCM model, conventional model) and two locations (Velenje, Koper).

5. Conclusion

The results presented illustrate the potential of PCM incorporation into plasters mixes to improve thermal properties while maintaining mechanical strength and provide valuable insights into the development of sustainable and energy-efficient building materials.

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1 Wang H. 2019.

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Hydraulic properties of experimental lime mortars with differently sized volcanic aggregates: Insights from a multi-analytical approach

1. Introduction

Mortars produced by mixing aerial lime with pozzolanic aggregates (natural or artificial) have been extensively used in the past for the construction of historical buildings[1-2]. In the Baroque built heritage of Catania (Eastern Sicily), volcanic materials from Mt. Etna eruptive activity have played a crucial role in the formulation of both bedding and rendering lime mortars. In particular, two types of volcanic aggregates, locally known as azolo and ghiara, have been widely employed during the intense reconstruction activity of the city in the 18th and 19th centuries following the devasting 1693 earthquake. Azolo, now referred as finely ground basalt, in its ancient meaning was an incoherent pyroclastic rock (volcanic ash), while ghiara is the product of a thermal transformation of palaeo-soils due to lava flows[3-4]. These two aggregate materials, peculiar to the Etna territory, served as the primary source of aluminosilicates for ancient mortar production. They were mixed with aerial lime in specific proportions, reacting in the presence of moisture to form stable binding hydrates, specifically calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH). In this study, experimental repair mortars have been designed for conservation and restoration purposes of historic masonry. Different formulations have been prepared by using a variable aggregate grain size to explore how it affects the binder/aggregate reactivity as well as the physical-mechanical properties of mortars.

2. Materials and methods

A ready-made commercial slaked lime has been used as binder. As for the aggregates, volcanic ashes from the 2002 eruptive event, have been collected at Piano Provenzana (in the northern side of Mount Etna volcano), while ghiara samples have been taken out at Cava Perniciano near the town of Belpasso (in the territory of Catania). The ancient recipe known from literature[5] has been used for the mortar preparation, in particular, a 3:1 aggregate/binder ratio was used for both azolo- and ghiara-based mortars. Two different formulations were prepared for each type: one with aggregate grain size in the range 2 - 0.063 mm (MC1 and MG1 series) and the other one also comprising the finer fraction < 0.063 mm (MC2 and MG2 series) (Table 1).

After 28 days of curing at room temperature, specimens underwent a multi-analytical program, including: mineralogical characterization (XRD), thin section analysis (POM), water absorption tests (by capillarity and at atmospheric pressure), accelerated degradation test by salt crystallization, uniaxial compression, and perforation resistance tests. In addition, a GIS-based image processing approach via the Quantitative X-ray Map Analyser (Q-XRMA) software[6] was applied to better investigate the hydraulic properties of

1 Belfiore et al. 2010.
2 Theodoridou et al. 2013.
3 Belfiore et al. 2022.
4 Belfiore et al. 2023.
5 Battiato 1988.
6 Ortolano et al. 2018.

Mortar type	Mixture ID	Grain size of aggregate	Aggregate/binder vol. ratio	H_2O amount
Azolo-based mortars	MC1	Φ ≤ 2 mm	3:1	10.10 %
	MC2	2 mm ≤ Φ ≤ 63 µm		
Ghiara-based mortars	MG1	Φ ≤ 2 mm		8.33 %
	MG2	2 mm ≤ Φ ≤ 63 µm		

Table 1. List of experimental mortar types and their characteristics

experimental mortars. X-ray elemental maps of two representative micro-domains for each mortar type were acquired at high resolution (about 2 µm pixel) and processed to assess the influence of aggregate grain size on the reactivity with the surrounding binder.

3. Results and discussion

The results of all investigations provided insights into the influence of aggregate composition and grain size on the physical-mechanical performance of examined lime mortars. On the whole, ghiara-based mortars exhibit better physical-mechanical performance than the azolo-based ones. Additionally, the image processing approach used revealed the distribution and quantification of hydraulic phases within the binder of the different mortar formulations. The adopted image-assisted analysis was carried out in two analytical cycles: the first one allowed to identify the constituent phases of mortars, while a second analytical cycle was focused exclusively on the binder.

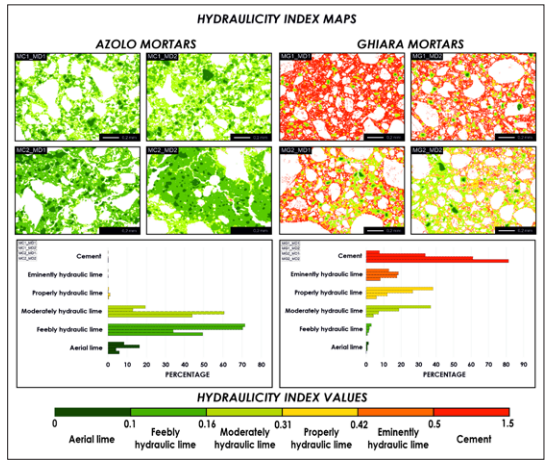

Figure 1. Hydraulicity index calculated within the binder obtained using the Q-XRMA results for the selected azolo and ghiara mortars micro-domains.

All samples displayed four chemically distinct zones which, however, are not directly comparable to each other due to different quantitative ranges for each element. The variability of the Hydraulicity Index (HI)[7] within the selected areas was also assessed (Figure 1) by using kernel density maps of the elemental maps classified during the first analytical cycle. On the whole, ghiara-based mortars exhibited higher HI values (mainly falling within the 0.31–1.5 range, corresponding to moderately hydraulic lime to cement) than the azolo-based ones (mainly falling in the 0–0.31 range, corresponding to aerial lime to moderately hydraulic lime). Furthermore, in both mortar types, specimens with fine-grained aggregate (MC1 and MG1) display averagely higher hydraulicity index than those with coarser aggregate grains (MC2 and MG2).

4. Conclusions

The experimental approach used highlighted that the aggregate grain size influences the reactivity of mortars. Specifically, the mortar specimens containing the fine-grained fraction (< 0.063 µm) exhibit higher HI values, certainly due to the increased reactive specific surface area. This is particularly evident in ghiara-based mortars, where the fine fraction promotes the hardening processes, reduces porosity and water absorption and improves mechanical strength. Conversely, in azolo-based mortars, the fine fraction has negligible impact on water absorption and compressive strength but delays hardening.

7 Boynton 1980.

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Restricted quantities - representative outcomes: proposed methodology for evaluating the effectiveness of consolidants on prehistoric earthen constructions

1. Aim of the study

This study presents a tailored methodology for evaluating the effectiveness of consolidation treatments on prehistoric earthen constructions using restricted quantities of original material. Addressing the fundamental conservation principle of minimal intervention, the proposed methodology balances analytical requirements with practical limitations of sampling archaeological artifacts.

Clays are susceptible to water induced weathering, especially in the presence of swelling minerals[1]. Water absorption results in volume increase and the production of strong stresses within the clay layers. Upon drying, water evaporates causing shrinking, while the repetition of wetting/drying cycles affects the cohesion of the internal clay structure and may lead to crumbling[2]. In the presence of swelling minerals, such as montmorillonite, stresses are higher and dimensional changes further constrains the physical integrity of the material[3].

Methods of measuring the response of earthen materials to moisture, rain, air abrasion are mainly reported for newly produced earth blocks or those derived from historic houses[4], where high quantity of sampling material is usually available. Soil characterization protocols have also been applied on historic earth blocks[5] of rectangular shape, where standardization is achievable and quantifiable[6]. Adapting these methods on archaeological earthen materials, where sample quantity is restricted, is challenging and could limit the potential of conservation studies. Additionally, the irregular shape of specimens and their variable state of preservation, even within the same batch of samples, requires mitigation actions for achieving useful and representative outcomes on the efficiency of consolidation or surface protection treatments.

Consolidants are applied for improving cohesion of constituents, enhance the internal structure of weathered materials and modify their microstructure, thus, affecting water absorption and evaporation. Surface treatment materials in contrast, affect wetting / drying surface properties of adobe structures[7] without affecting microstructure and cohesion. Finally, swelling inhibitors interact with clay minerals and modify interaction with water without affecting microstructure or surface properties. Therefore, it is essential to characterise the clay mineralogy and understand the weathering mechanisms that affect preservation first, before deciding on the most appropriate testing protocol.

1 Panagiotou et al. 2022, 184.
2 Stefanis et al. 2010, 4.
3 Michalopoulou et al. 2020, 229.
4 Rescic et al. 2023.
5 Fabbri et al. 2022.
6 Hart et al. 2021, 3.
7 Stefanis et al. 2010, 2.

2. Methodology

The methodological scheme concerns the study of mudbricks and clayey building materials from three prehistoric archaeological sites in Greece and follows a systematic decision tree initiated by comprehensive mineralogical characterization via X-ray diffraction (XRD) analysis and infrared spectroscopy (FTIR) to identify, along with small scale laboratory tests, the presence of swelling clays. This critical distinction guides subsequent testing protocols: materials containing swelling clays are prioritized for testing swelling inhibitors, while non-swelling clays are evaluated with cohesion-enhancing consolidants. Microstructure, texture and elemental composition are assessed through Scanning Electron Microscopy coupled with Energy Dispersive Analysis (SEM-EDX) providing further insights into the state of preservation. FTIR assesses mineralogical alterations, swelling modification and depth of consolidant impregnation.

The hygric properties of clays before and after application of conservation materials are measured by methods tailored to the specifications of the materials under study, mainly on their available quantity. Methodological challenges are addressed through: (1) comparative testing of reconstituted clay specimens of defined dimensions to evaluate consolidant efficacy across different clay mineralogies, adapting protocols for soil testing[8](fig.1a); (2) direct application of selected consolidants on original fragments of irregular shape to include preservation state assessment (fig.1b); and (3) adapted surface testing, such as the pressure spray method, the Geelong method for soil and rammed earth and the measurement of the transportation of moisture[9] on irregularly shaped authentic samples (fig.1c).

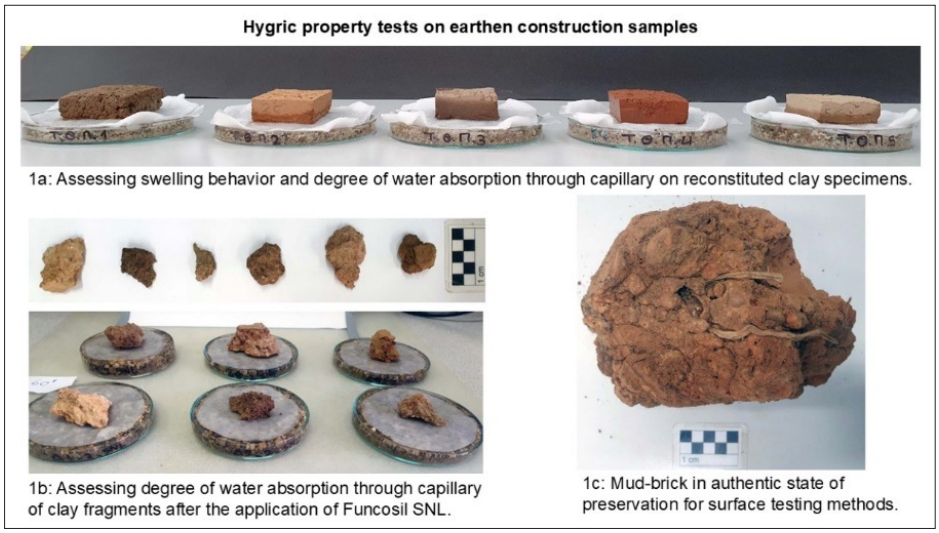

Figure 1: Modified hygric property tests on 1a) reconstituted clay specimens, 1b) original clay fragments of small size and 1c) mud-brick sample of poor state of preservation.

3. Outcome

The interpretation of results from testing different types of conservation products in different types and typologies of specimens, along with the experience retrieved through literature, allows a thorough review of benefits gained and limitations faced. Overall, the adaptive methodology proposed enables conservators/restorers and conservation scientists to retrieve reliable and representative outcomes on the effectiveness of different conservation interventions, while respecting the irreplaceable nature of archaeological materials. Therefore, it is considered as a practical, yet reliable framework for decision-making when working with restricted quantities of prehistoric earthen materials.

8 D4546-14.
9 NZS 4298:1998.

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Compatibility of dolomitic lime renders with calcium-based consolidants

The consolidation of lime-based renders plays a crucial role in preservation of built heritage. Wall paintings are particularly vulnerable due to their fragile nature of lime-based substrates and their susceptibility to deterioration. While calcium lime renders are commonly studied, the consolidation of wall paintings produced with dolomitic lime has not been addressed yet. During carbonation, beside calcium phases, several magnesium phases occur in dolomitic lime mortars, such as brucite and magnesium hydroxide carbonates[1]. The use of dolomitic limestone in lime production is historically well known in the north and south of Italy but it is also documented in France, Germany and United Kingdom, especially between the 16th and the 17th century[2]. In Slovenia, the use of dolomitic lime is documented especially for the wall paintings of Baroque period[3]. Dolomitic mortars are however considered less durable than calcium-based mortars due to their higher water retention and greater tendency to shrink during drying, which can result in the formation of microcracks. In addition, their uneven carbonation process may compromise the stability and adhesion of the paint layer. Under fluctuating humidity conditions, dolomitic mortars are particularly susceptible to the formation of magnesium salts, which can lead to efflorescence, pigment alteration, and mechanical damage to the surface. Conservation of wall paintings executed on dolomitic substrates presents further challenges, as many inorganic consolidation treatments are chemically incompatible with high magnesium content, limiting effective intervention options. In recent years, improvements in material science have focused on developing compatible consolidants to enhance the durability and stability of lime-based substrates[4]. Carbonate-based consolidants are characterised by efficient penetration into porous materials and the ability to strengthen fragile substrates.

This research evaluates the effectiveness of three consolidants — calcium acetoacetate (CFW), Nanorestore (NR), and NanoLaq (NL) individually and in combinations. The reason for choosing these consolidants lies in their complementary mechanisms: nano-lime-based consolidants (NR, NL) contain calcium hydroxide particles that boost the

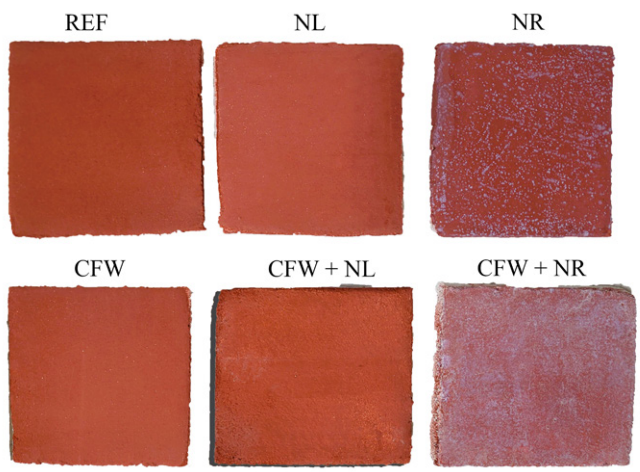

Figure 1. Consolidation of render substrates painted with red ochre with various carbonate-based consolidants

1 Bläuer-Böhm & Jägers 1996.
2 Vecchiatini 2003.
3 Kramar & Mirtič 2008.
4 Pondelak et al. 2020.

formation of calcium carbonate in case of CFW consolidant, while released CO2 from CFW accelerates the carbonation process, potentially improving the effectiveness of both consolidants. For this purpose model substrates were made using red and blue pigments (red ochre and azurite) to replicate the characteristics of historical wall painting and to simulate traditional secco technique. The render composition consisted of dolomitic lime and ground carbonate aggregates. Samples were treated with CFW, NR and NL, applied individually and in combination (CFW followed by NR, CFW followed by NL, NR followed by CFW and NL followed by CFW). To track changes over time, samples were analyses in different periods (7, 30, and 90 days). Non-invasive methods included microhardness testing, ultrasonic velocity measurements and micro-invasive method as the drilling resistance measurement system (DRMS) to measure penetration depth and increase in mechanical properties after the consolidation. Spectrophotometry was used to monitor colour changes after the application of consolidant. The results show that the colours are slightly darker after consolidation with CFW and the combination of CFW and NL. In contrast, consolidation with NR and the combination of CFW and NR results in slightly lighter areas (white spots), while there is no significant colour change after treatment with NL. The measurements of hardness show that in most cases the values are higher compared to the untreated substrate. Similarly, DRMS measurements show increased values for CFW and NL alone, as well as for the combination of CFW with NR. The results contribute to better understanding of dolomitic lime interaction with carbonate-based consolidants and sustainable practices in preservation of wall paintings.

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Innovative Eco-friendly Additives for Enhancing the Self-Healing Properties of Historic Building Renders

1. Introduction

Over the last few decades, the scientific community has been studying the autogenous properties[1] of mortars and concrete to enhance the durability of both new and historic buildings[2]. This property, also known as self-healing, is the ability of materials to repair themselves after being subject to a physical stress. Lime-based mortars are among the most commonly used materials in historic buildings, valued for their flexibility[3] and excellent vapour permeability and properties that regulate air humidity[4]. The self-healing capacity of mortars is significantly influenced by various factors, including the composition of the matrix, the age of the conglomerate, the age and extent of the damage, internal stress, curing conditions, and prevailing microclimatic conditions such as humidity and temperature[5].

2. Materials and methods

2.1 Materials

This study aims to evaluate the self-healing properties of a commercial render based on pozzolanic hydraulic lime and to propose innovative additives that could potentially enhance its self-healing behaviour. In particular, we investigated the use of natural hydraulic lime (NHL) coated with organic polymers and rice-derived materials as additives. The coating keeps the lime granules inert during the initial hardening phase, releasing the reactive binder only after a mechanical stress occurs, facilitating the self-healing process. Rice-derived materials are included in the study due to their content of SiO2 and potential for enhancing self-healing.

2.2 Methods

A reference render was first produced to analyzeanalyse any potential self-healing abilities and then to compare the possible benefits of the new additives' inclusion. The additives were added to the mix in a range from 0.5 % to 6 % by weight. As suggested by the producer, we added the water to the mix at 18 - -20 % by weight. To assess the self-healing property, we conducted compressive strength tests following the BS EN 1015-11:2019 standard. After an initial curing period of 28 days, – during which the mock-ups were kept in mould in high-humidity chamber (relative humidity (RH) 90 ± 5% and temperature (T) 23 ± 2 °C) for 7 days, and then in microclimate laboratory (RH 55 ± 5% and T 21 ± 2 °C) for the remaining 21 days – we tested the control group using a dynamometer to evaluate the maximum compressive force required to achieve complete failure. We set the dynamometer to a loading rate of −0.03 N/s and a loading

1 De Souza, Sanchez 2023.
2 Tariq, Jafaar 2024.
3 De Nardi et al. 2017.
4 Damle, Khatri, Rawal 2022.
5 De Nardi (n. 3); Damle (n. 4); Qureshi, Al-Tabbaa 2020.

gradient of 0.01 N/s/mm², as in lime-based mortar studies found in the literature. Then, we applied 50% of the maximum force for each formula to reach the half-break for all mock-ups, choosing this value to avoid accidental full breaks. Subsequently, we split all mock-ups into two groups to allow for self-healing. The first group (4h) was immersed in water for four hours and then left at microclimate laboratory. The second group (HH) was placed in a high-humidity box (RH 90 ± 5%) at the same room temperature. Both groups were kept for curing and self-healing for an additional 28 days, reaching a total age of 56 days. After this period, we carried out the final compressive strength test until complete failure occurred.

3. Results and discussions

Although the maximum compressive strength of the OCG and RD groups was lower than that of the control group after the initial 28-day period, the mock-ups with OCG additives showed higher compressive strength than both the control group and the RD group after the self-healing period, at 56 days of age. Data analysis showed good self healing properties, especially with the 4h curing method (Figure 1), except for the RD group.

These results from our ongoing study have been a good starting point for the mechanical characterisation of the material. We have already planned to continue with an in-depth investigation of these additives to analyse their influence on freeze-thaw resistance, waterproofing, water absorption, and thermal insulation properties, if any. Hopefully, these studies will contribute to improving the weathering and climate change resilience of historic buildings by using eco-friendly and sustainable materials.

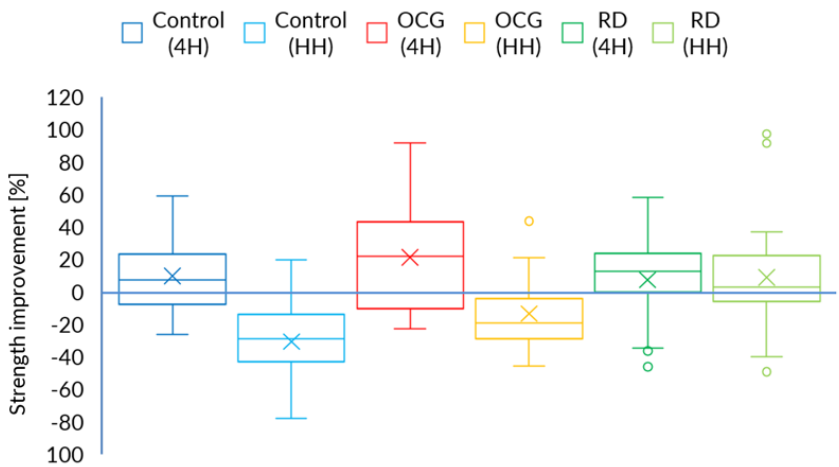

Figure 1. This box plot shows the degree of improvement in compressive strength, expressed as a percentage relative to control groups of the same age. Control: mock-ups without additives; OCG: Organically Coated Granules; RD: Rice-Derived; 4h: cured in water for the first 4 hours to induce the self-healing, then stored in a microclimate laboratory for 28 more days; HH: 28-day curing in a high-humidity chamber to induce the self healing

Acknowledgments

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Biogenic mineral precipitation and self-healing in lime-based mortars: showcasing its potential through the Healing Masonry prototype

The Healing Masonry prototype investigates the application of emergent biological self-healing systems to masonry materials through Microbially Induced Calcite Precipitation (MICP) or biomineralisation. MICP is a naturally occurring process in living organisms where precipitation of minerals occurs due to the interaction of metabolic by-products of microorganisms and ions present in that environment.
Biomineralisation has been explored for consolidating porous materials, such as soil[1], building stone[2], and concrete[3]. The potential of microbes to induce calcium carbonate precipitation has also been studied as a biological self-healing technique for developing materials capable of sensing and repairing damage[4]. However, the technology remains largely unexplored for cementless environmentally friendly materials, such as building stone, lime-based mortars and earth-based composites, which are commonly found in masonry and heritage structures globally. Such materials are bioreceptive and suitable for biomineralisation[2-5-6]. Unlike many conventional heritage conservation methods, biomineralisation-based treatments are inherently compatible with traditional materials[7], require lower energy input, and can be self-regenerating, significantly reducing intervention frequency and environmental impact. Previous and ongoing research has shown evidence that MICP could be successfully used to develop self-healing masonry materials[2-5-6]. In this project, Sporosarcina pasteurii have been used for inducing biomineralisation and provide self-healing properties to lime-based construction composites.
In this project, Sporosarcina pasteurii have been used for inducing biomineralisation and provide self-healing properties to lime-based construction composites.
In its first phase, the project introduced red-dyed lime mortar blocks (natural hydraulic lime mixed with silica sand fine aggregates at a ratio of 1:3), treated with the biological self-healing ingredients containing the bacterium Sporosarcina pasteurii and the nutrient solution[5]. The blocks were subjected to 28 wet–dry cycles, during which visual documendation recorded progressive development of calcite precipitation accompanied by a noticeable colour transition from red to white. Fissures and textured surfaces encouraged early deposition, revealing patterns of mineralisation over time. The samples modular display at the the Hub's for Biotechnology in the Built Environment (HBBE) experimental house the 'OME' was designed to invite hands-on interaction, encouraging the public and professionals alike to observe the materials evolution and assess physical changes. The 'OME' is located in the heart of Newcastle University campus, Newcastle Upon Tyne, UK, where researchers come together to collaborate, test and demonstrate their technologies at large scale, as well as to showcase their work to the industry and to the public. Rather than concealing weathering and the changes from natural processes, the Healing Masonry prototype calls attention to the distinction between the 'alive' and the inert parts of the building, communicating

1 Harbottle and Al-Tabbaa 2008.
2 Theodoridou et al. 2021.
3 Van Tittelboom et al. 2010.
4 Joseph et al. 2010.
5 Theodoridou et al. 2023.
6 De Nardi et al. 2019.
7 De Muynck et al. 2010.

the biological self-healing as a living repair process that improves the materials' physical condition while embracing the impact of time passing in a real building context.
The second phase expands the scope to real-world applications. It involves the fabrication and installation of tile units with varying levels of biological treatment, positioned on the façades and interior walls of the OME. The materials are monitored under natural weathering in outdoor and indoor environments, with visual documentation and in-situ testing methods including the Drilling Resistance Measurement System (DRMS), water absorption and surface cohesion. Microbial community evolution over time is also tracked through DNA sequencing.
This project demonstrates how biologically driven reinforcement can operate outside of laboratory settings, expanding our understanding of performance under real-world conditions. In doing so, it not only contributes new technical insights into self-healing mortars, but also advocates for a broader reconsideration of how materials science, conservation, and sustainable design might intersect.

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MOHAMED-AYMEN KETHIRI, CRISTINA TEDESCHI

Development and Characterization of a Restoration Material Using Local Resources (Gypsum-Lime/Date Palm Fiber): Case Study of the Si El Haoues Museum in Algeria

1. Introduction

The conservation and restoration of heritage buildings is an essential aspect of cultural preservation, particularly in regions where historical structures represent significant cultural and architectural value. The M'chounech "Si El Haoues" museum, located in the Biskra region of Algeria, stands as a valuable testament to the rich history of the area, reflecting traditional construction techniques and materials. However, like many heritage sites, it faces deterioration due to environmental factors and material degradation over time. Effective restoration efforts require the use of materials that are not only compatible with the original construction but also environmentally sustainable and locally available.

Lime and gypsum-based materials have been traditionally used in the construction and restoration of historical buildings in north Africa due to their availability and compatibility with local building materials and techniques. The inclusion of agricultural waste such as wheat straw[1], date palm fibre[2], coconut fibre [3] and hemp fibers[4] has been explored as a means to enhance the mechanical and thermal properties of these materials[5], 6. The use of lightweight materials in the restoration of architectural structures has gained significant attention in recent years. Similarly, the potential use of date palm wood residues as a reinforcing agent in composite materials has gained increasing attention.

Recent studies have explored the potential of bio-composite materials combining gypsum plaster with date palm fibers (DPF) for sustainable construction. These composites demonstrate improved thermal insulation properties, with reductions in thermal conductivity of 22%, 26.24%, to 37.65% compared to neat gypsum plaster. However, compressive strength may decrease due to poor adhesion between fibers and matrix. Chemical treatments can improve fibre-matrix adhesion and overall composite durability.

In this study, the suitability of a gypsum-lime composite reinforced with date palm (DP) fibers was assessed for the restoration of the M'chounech 'Si El Haoues' museum in Algeria. The integration of natural fibers like DP into traditional construction materials offers an environmentally sustainable solution. This evaluation aimed to assess the composite's physical and thermo-mechanical properties to determine its effectiveness in restoring heritage buildings while preserving structural integrity and aesthetic qualities. Characterization tests, including compressive strength, thermal emissivity, and moisture resistance, were conducted. Various mortar compositions were prepared with different DP proportions (0.7% and 1.4%) and particle sizes (0.25 mm and 1 mm). Finally, the observed results demonstrated that the lightness of the gypsum-lime composite was improved by the addition of date palm fibre, which contributed to the formation of pores within the material, as seen in the density, porosity, and ultrasonic test results. However, the mechanical properties were negatively impacted by the addition of date palm fibre. Additionally,

1 Kethiri et al. 2010.
2 Danso et al. 2020.
3 Parcesepe et al. 2021.
4 Bourbia et al. 2023.
5 Adamu et al. 2022.

the thermal properties were improved, as the thermal conductivity and the bulk density were lowered, making the material more insulating than its neutral state and suitable for restoration application.

2. Materials and Methods

2.1 Plaster of the M'chounech museum

The Si El Haoues Museum in M'chounech, Biskra, is a key cultural site showcasing traditional architecture. In a previous study, we analyzed the museum's plaster to develop a compatible restoration material. The plaster showed a density of 1267.9 kg/m³ and a thermal conductivity of 0.884 W/m·K, guiding the creation of a suitable restoration mix.

2.2 Gypsum

The gypsum used in this study was obtained from the GCI company in Biskra city in Algeria. According to the company's recommendations, this type of gypsum is preferably used with a water/gypsum ratio (w/g) which can vary from 0.6 to 0.8.

2.3 Lime

Lime is a type of lime that is derived from limestone containing natural impurities of clay and other minerals. lime comes in several different grades. The lime used in this study is from Spadaro company.

2.4 Sand

The characteristic of CEN Standard Sand is its specific grain size distribution. The maximum moisture content is 0.2%. The sand is portioned in bags of 1,350 (± 5) g. The mortar prisms for compressive and flexural strength testing are produced with an aggregate within 0,5mm.

2.5 Date palm fiber

The date palm component investigated in this study was obtained from leaves, particularly leaflets (Figure 1), harvested in the geographic regions of Tolga and Biskra in Algeria. The raw material used in this study was processed according to the procedure used by Kethiri et al.

Gysum (g)	Lime (g)	Sand (g) (0,5mm)	Date palm fiber (g)	Concentration[Y] (%)	Dimensions[X] (mm)	Water (g)	Specimens' names
350	450	400	\	\	\		G-L
344,4			5,6	0,7	0,25		G-L-0.7-DP-0.25
					1		G-L-0.7-DP-1
338,8			11,2	1,4	0,25		G-L-1.4-DP-0.25
					1		G-L-1.4-DP-1

Table 1. Composition and names.

3. Results and discussion

In this study, a restoration material composed of lime, gypsum, and reinforced with date palm fibers was prepared and tested. The properties of this material were compared with samples taken from the Si El Haoues Museum in M'chounech. The results showed that the new material exhibited characteristics like those of the original plaster used in the museum.

As illustrated in Figure 1, the values of density, apparent density, and porosity were found to fall within the same range as those measured in the museum samples. These results confirmed the compatibility of the new mixture with the original material in terms of physical properties.

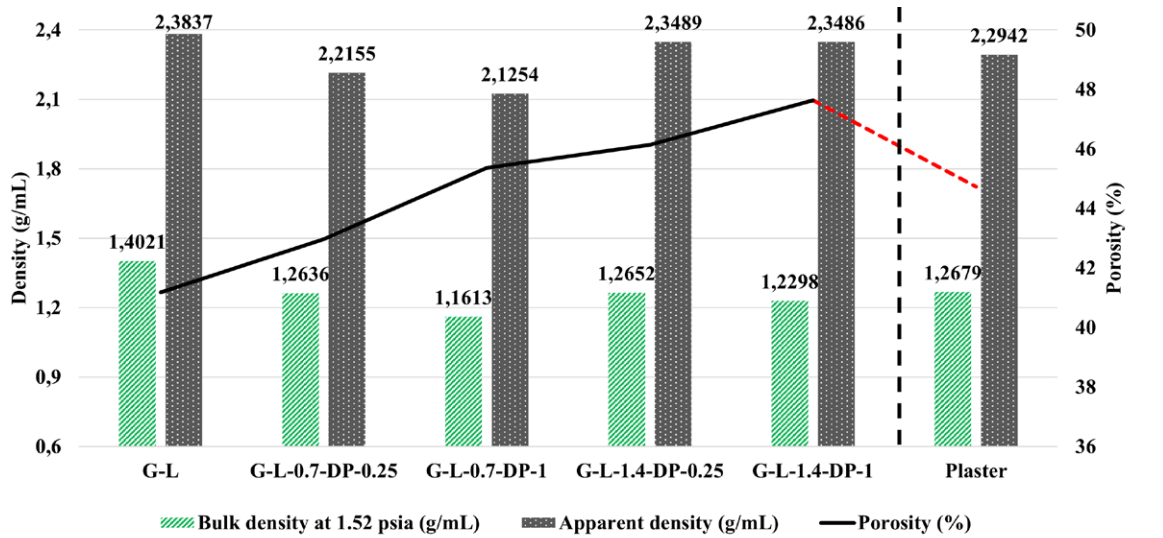

Figure 1. Comparison of the densities and porosity of the prepared specimens with the plaster sample.

Mechanical characterization was also carried out, and although the results demonstrated acceptable performance, the most significant improvement was observed in the thermal behaviour of the material. The thermal conductivity was found to be lower than that of the original plaster, indicating better insulation properties, which is beneficial for the restoration of traditional buildings in warm climates.

Acknowledgments

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CRISTINA TEDESCHI, MOHAMED-AYMEN KETHIRI

Integration of nanocellulose into a composite material based on lime reinforced with cork: Experimental study

1. Introduction

The integration of nanocellulose into lime-based composite materials reinforced with cork has shown promising results in enhancing mechanical properties and sustainability. This experimental study highlights the synergistic effects of combining these materials, leading to improved performance in various applications.

Nanocellulose, derived from natural sources, has emerged as a promising additive in the development of fiber-reinforced cement composites. Its incorporation enhances mechanical properties and sustainability, making it an attractive option for construction applications1. The use of natural fibers, including cork, in composite materials has been extensively studied, highlighting their potential to improve the performance of lime-based matrices 2. Cork, known for its lightweight and insulating properties, complements the characteristics of nanocellulose, potentially leading to composites with superior thermal and acoustic performance.

While the integration of nanocellulose into lime-cork composites shows significant potential, challenges remain in optimizing the dispersion of nanocellulose and ensuring consistent performance across different applications. Further research is needed to address these issues and fully realize the benefits of these innovative materials 3.

This study explores the development of a sustainable bio-composite material tailored for architectural restoration, using hydraulic lime (HL) combined with cork and nanocellulose. Five mortar compositions were investigated: a reference mix with 100% sand, a mix with 100% cork, a hybrid mix with 50% cork and 50% sand, and two mixes combining 100% cork with nanocellulose at 0.25% and 0.5% by weight. The physical, and mechanical properties of these formulations were evaluated through porosity, density, ultrasound transmission, and mechanical strength tests. The results demonstrate that cork significantly reduces the density of the material, making it lightweight, while the incorporation of nanocellulose improves mechanical performance. These characteristics are particularly advantageous for restoration applications, where lightweight materials with adequate mechanical strength are highly desirable. This research highlights the potential of eco-friendly composites using agricultural and industrial by-products, contributing to sustainable and effective restoration practices.

2. Materials

2.1 Lime

Natural Hydraulic Lime (NHL) is a type of lime that is derived from limestone containing natural impurities of clay and other minerals. NHL comes in several different grades.

2.2 Cork

Cork is a sustainable, lightweight material with excellent thermal and acoustic insulation properties. It is used in construction for insulation, flooring, and eco-friendly mortars, enhancing energy efficiency and comfort while supporting green building practices. The cork used in this study is from Sace.

2.3 Sand

The characteristic of CEN Standard Sand is its specific grain size distribution. The maximum moisture content is 0.2%. The sand is portioned in bags of 1,350 (± 5) g. The mortar prisms for compressive strength testing are produced with a mixture of 450 (± 2) g cement, 225 (± 1) g water and one bag of 1,350 (± 5) g CEN Standard Sand.

2.4 Nanocellulose

Nanocellulose liquid is a strong, lightweight, and eco-friendly material that enhances building materials by improving strength, flexibility, and durability. It supports sustainable construction and is ideal for reinforcing mortars, plasters, and coatings.

Lime (g)	Sand (g)	Cork (g)	Nanocellulose (g)	Names	
450	1350	\	\	Lime	Lime
	517,2	30,5		Lime 50% CORK	Lime_0.5_Cork
	\	61		Lime 100% CORK	Lime_1_Cork
			101,35	Lime 100% CORK+0,25 NCC	Lime_1_Cork_0,25_NCC
			101,35	Lime 100% CORK+0,5 NCC	Lime_1_Cork_0,5_NCC

Table 1. Composition and names

3. Results and Discussion

The mechanical behaviour of the different formulations was evaluated through flexural and compressive strength tests. The reference composition (Lime) exhibited the highest values, with a flexural strength of 1.43 MPa and a compressive strength of 4.23 MPa. Upon the addition of cork, a significant reduction in strength was observed. The formulation with 1% cork (Lime_1_Cork) showed the lowest values, with a flexural strength of 0.28 MPa and a compressive strength of 0.61 MPa. This decline is consistent with previous observations, where increased fibre content or particle size led to a drop in mechanical performance.

However, when nanocellulose (NCC) was introduced into the mix, a partial recovery in strength was noted. The Lime_1_Cork_0.5_NCC composition, for example, reached a flexural strength of 0.55 MPa

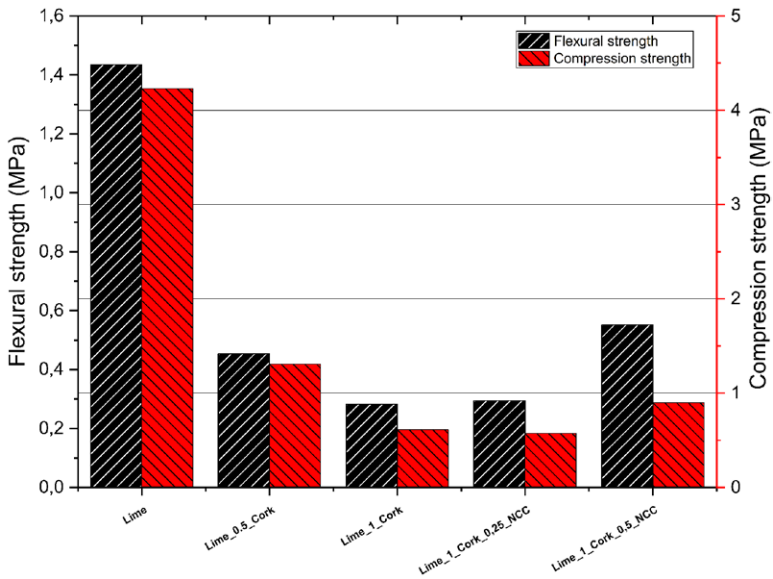

Figure 1. Mechanical proprieties of the specimens studied

and a compressive strength of 0.89 MPa. These results confirm that while cork addition tends to reduce mechanical resistance, the incorporation of nanocellulose helps to improve the performance, especially in flexural strength. Overall, the mechanical properties remain sensitive to both the type and amount of additive used.

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RUBEN PAUL BORG

Innovative high-performance mortars for the conservation of a Reinforced Concrete Water Tower

Abstract
The Reinforced Concrete Wate tower, constructed in the first half of the 20th Century, was restored using innovative mortars developed to address the requirements of the structure. The restoration was based on research and development of innovative high-performance materials together with their application, new advanced techniques in restoration of reinforced concrete and the development of a smart sensor network system for the durability and structural health monitoring of the structure. The extensive degradation of the structure presented significant challenges in the recovery of the industrial heritage monument and necessitated complex restoration process and the development and application of advanced mortars. The project set a methodology for appraisal and conservation of reinforced concrete heritage structure including the development and application of mortars to address the conservation strategies in concrete.

Figure 1. Left – detail of the relief of Faida; right - SEM-back scattered electron image of the stratigraphy observed in one of the fragments collected from the relief of Faida, in which the dolomitic rock on which the reliefs were carved is covered by layers of very fine-grained calcite

Water Tower Conservation
The reinforced concrete water tower was constructed in the 1930s to serve the needs of the Public Abattoir in Malta. It is the only structure of its type and size in the Maltese Islands and is considered as an important Industrial Heritage monument. The Water Tower consists of a reinforced concrete structure c.15 m high with a c. 10m diameter tank having a capacity of 400 cubic m. The tank consists of a shell structure with a cylindrical drum resting on a truncated conical structure with a dome at the base and ring beams, supported on 12 slender reinforced concrete columns. The structure had been considered for demolition in 2010 as a result of severe degradation and significant loss of section particularly of the shell structure of the tank. The case for the conservation of the unique water tower was made by the Uni-

versity of Malta, leading to a strategic conservation programme. The project required the development of new methodologies in the emerging field of reinforced concrete conservation, which had to be designed for the complex structure whilst effectively addressing the severe degradation.

Conservation Project

The complexity of the conservation project and innovative solutions which had to be developed, required a comprehensive Management Framework, which could ensure the recovery of the industrial heritage monument. The intervention was conducted on the basis of scientific restoration methodology and included key strategic steps: archival research and documentation, the appraisal of the industrial heritage structural through mapping of deterioration, research campaigns in the assessment of the materials and the structure including, materials non-destructive assessment, materials testing, structural microtremor analysis and numerical structural modelling and scenario testing to optimise repair and strengthening interventions. The methodologies for restoration were planned depending on specific needs of the structure. New complex techniques for restoration were developed and applied in the restoration project including electro-chemical chloride extraction, re-alkalisation of reinforced concrete, epoxy injection and polymer concrete patch repair and the use of corrosion inhibitors, re-integration of the structure and improvement of bond between materials, using specialist techniques.

Advanced Mortars

The recovery of the structure could only be made possible through specific solutions which had to be developed Malta, including new advanced materials. Ultra-high performance concrete (UHPC) with increased ductility, self-healing and self-compacting properties, based on nano-additives was developed and tested at the University of Malta. UHPC was then applied and tested on replica columns and eventually applied for the construction of jackets to the columns. Carbon-textile composite reinforced high-performance concrete was similarly developed and tested for the effective strengthening of the tank. The research conducted included the development and assessment of the mechanical and durability properties of the new materials, their performance with respect to the applications for which these were designed and the assessment of the bond performance when applied onto the existing structure.

Restoration Intervention

A site production facility was set up, and replica structures were created including columns and shell wall elements to enable the testing of materials and application of technologies on these structures, prior to intervention on the Industrial heritage structure proper. An advanced sensor network system for monitoring over time was designed, based on durability monitoring including new sensors developed by the University of Malta, structural health monitoring and environmental monitoring. The advanced system, based on 150 sensors and the monitoring station enables the long-term monitoring of different parts of the structure when in use, ensuring maintenance and timely restoration in the future. The Project presented key challenges in materials engineering and the development of novel ultra high-performance materials; sensor network systems for advanced structural health monitoring; and advanced restoration technology for degraded concrete industrial heritage structures. These areas are brought together to address the conservation of the water tower, through a new Technology Platform created as a new University of Malta Research and Training Station for the development of advanced materials and sensor systems, structural repair and the conservation of industrial heritage structures.

Conclusion

The structure was brought back into operation as Industrial heritage in use, following an intense validation exercise through the monitoring of structural behaviour during the filling in operation of the 400

cubic metre tank. It has been reintegrated as a useful asset within the Public Abattoir facilities. The Water Tower stands as key representative of the Industrial Heritage in the Maltese Islands which, until now, has been largely ignored. The structure which was set for demolition in 2010, has been restored through advanced engineering solutions. innovation in high-performance materials and sensor systems, with potential for wider applications and interventions. The complex restoration has led to its Scheduling as a Grade 1 National Monument.

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STEFANO AGNETTI, RICCARDO LIBEROTTI, MATILDE PAOLOCCI, VITTORIO GUSELLA

Innovative Materials for the Consolidation and Repair of Historic Renders and Mortar-Based Elements

1. Introduction

Historical mortars represent a meeting point between tradition and innovation, where scientific research and project-based practice come together to find effective solutions in the conservation of architectural heritage. It is in this perspective that the agreement between the Department of Civil and Environmental Engineering of the University of Perugia and the Kimia S.p.A., a company with decades of experience in the production and application of structural strengthening systems, started. The aims of this ongoing collaboration is the development of new products compatible with the esthetical and material features recurring in mortar-based elements marking historical buildings (e,g,, renders, decorative apparatus etc.).The first stages of the research, object of the present contribution, are connected to direct design and implementation experiences concerning two monuments in the city centre of Perugia: the 14th-century Cattedrale di San Lorenzo and the 13th-century Fontana Maggiore, both located in Piazza IV Novembre (figure 1a). The strategies adopted respected the history and identity of the site, favouring the use of materials consistent with the original ones, in order to preserve the material and constructive continuity of the historical buildings' layout. Indeed, through careful sampling and experimental testing of existing materials (figure 1b), the plaster and lime-based mortars to be used in punctual interventions were identified, such as the mix designs for repointing the historic masonry walls of the aforementioned church. In particular, laboratory analyses were focused on evaluating the physical, mechanical, material and colour properties of the sample in order to define and produce mix designs suitable for their repairation and reintegration.

2. Experimental campaign

In the absence of specific codes and procedures for the experimental test on materials for plasters, finishings and decorative apparatus, the European standard BS EN 1015-11:2019[1] was adopted, even if intended for mortars, in order to give repeatability to the research. Indeed, the mixtures under analysis are comparable to mortars in terms of features, proper of artificial stone category of materials, with mechanical properties and degradation phenomena similar; as reported in the Italian standard UNI 1182:20062[2]. The experimental campaign, still ongoing and with new tests already planned, will be conducted using a numerically controlled machine, capable of monitoring the damage evolution during mechanical characterisation campaign (e.g. three-point bending and compression tests)[3]. Different mixtures will be tested both traditional[4] and innovative in order to compare the results from different respects[5-6] evaluating the

1 BS EN 1015, 2019
2 UNI 1182, 2006
3 Liberotti, Riccardo; Amer, Valeria; Gusella, Vittorio 2025
4 Liberotti R., Cluni F., Faralli F., Gusella V. 2022
5 Malomo D., Coccia S., Calandra M., Vintaloro R., Agnello S. 2024
6 Pizzo S., Fregonese L., Gottardi C., Nobile R. 2024

structural performances also in relation with compatibility and reversibility issues. The testing on each type of mix design will be carried out on at least three samples, according to standard dimensions and geometry (e.g., 16×4×4 cm for the bending tests), made at the same time and presenting the same curing period.

3. Conclusions and future perspectives

Starting from the direct experience on two relevant case studies, the research is focused on the analysis of mortar-like mixtures for the realization of interventions on the architectural heritage. While respecting the artisanal dimension of the restoration practice, new mix designs will be studied to make them industrially reproducible on a larger scale and to be in line with actual interventions criteria and codes. A comparative experimental campaign is ongoing to ensure consistency of mechanical performance, ease of production and reliability of application through targeted control of the composition elements and of the production process.

New tests are planned considering both traditional lime-based mortars and innovative formulations with environmentally friendly additives (e.g., lime–eco-pozzolan blended mix designs) in a seamless dialogue between academic and industrial research and development.

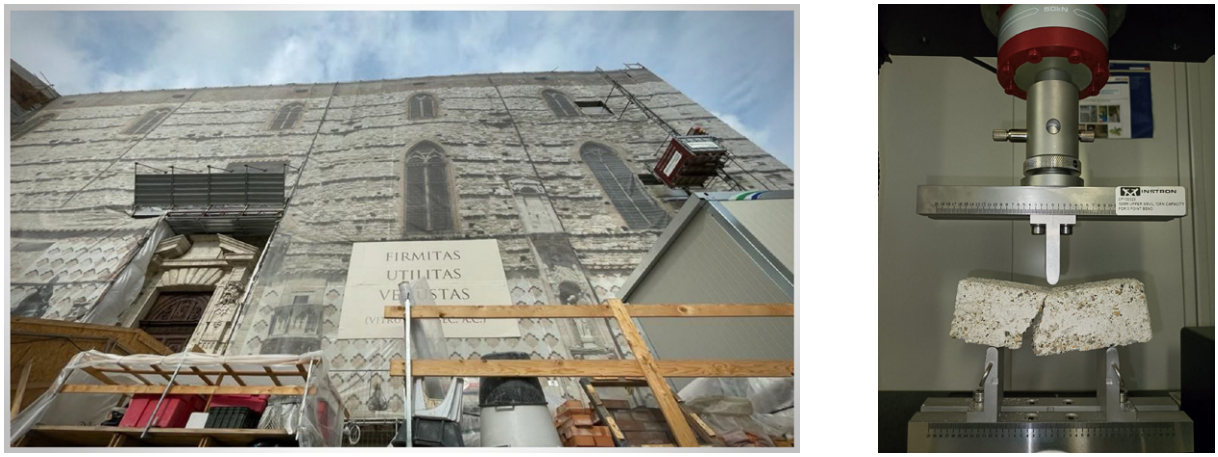

Figure 1. (a) Cattedrale di San Lorenzo of Perugia during the restoration works in 2024. Example of the three-point bending tests on one of the plaster mortars tested during the experimental campaign.

Figure 2. Details of the innovative plaster application on the San Lorenzo Cathedral of San Lorenzo during the restoration works.

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Topic 9

Repair mortars and grouts. Requirements and design. Compatibility issues. Durability and effectiveness. Adequacy of testing procedures

EK MALIN, STRANDBERG PAULIEN, BALKSTEN KRISTIN

Lime mortar - Strength over time

1. Introduction

It is generally accepted that the strength of lime mortars increases over time[1]. However, according to both current and previous standards, the strength of lime mortars is to be measured only after 28 days, which is in accordance with cement testing standards. Since there are no requirements for measuring lime mortar strength at time periods past these 28 days, no comparisons can be made to other lime mortar strengths at later times. This is one of the reasons why we chose to investigate the strength of lime mortars and the effect of ageing on strength development, after this initial period of 28 days.

In the research field of cultural heritage conservation, there is a need to use sustainable lime mortars in restoration projects in which lime mortars are compatible with the existing materials. This is particularly true when traditional, authentic lime mortars with long durability are required. When the strength is measured after 28 days, lime mortars may appear weaker than they will be in time, when they have fully hardened. This also means that the effects of ageing on strength development and therefore their strength over time may be considerably higher than anticipated.

The purpose of this study was to gain an understanding of the effects of ageing on the strength development of lime mortars by means of laboratory measurements. With a greater understanding of the long-term properties of building limes and their expected durability over time, more informed choices regarding the choice of lime mortar could be made. Knowledge regarding strength of traditional local lime mortars could promote the use of these materials with good durability compared to modern standard mortars. Similarly, information on their strength development over time will make it easier to make informed choices regarding hydraulic lime mortars used in restoration works. These limes might have a strength development over time that is stronger than anticipated and therefore not compatible with the older, existing lime mortars.

To measure flexural and compressive strength of the lime mortars, the European standard EN 1015-11[2] with its established method has been used. To determine the effect of ageing on the strength development of the lime mortars, the strength tests were performed at intervals past the 28-day period mentioned in the standard. Tests have been carried out at five different mortar ages, up to two years after preparing the specimens. The carbonation depth was also measured at the different time intervals to investigate the relationship between carbonation and strength development. A detailed description of the approach is described by Ek in which the results for the first six months are also reported[3].

2. Materials and Methods

Binder-rich lime mortars have been chosen that are similar to historical lime mortars as the results of the study were intended for use in the field of cultural heritage conservation. The mortars were based on

1 Apostolopoulou et al. 2021; Moropoulou et al. 2005.
2 European Committee for Standardization [CEN], 2019.
3 Ek, 2023.

traditionally produced Swedish hydraulic lime as well as industrially produced hydraulic lime. A total of 12 different mortars were examined.
The mortars were produced with a volume ratio of 1:1.5 (lime:sand), except for the reference mortar, which was a standard lime-cement mortar where ratio 2:1:12 was used. To ensure that all mortars had a similar consistency, the amount of water added to the different lime mortars was tested beforehand using standard EN 1015–4[4] as a guideline. Lime mortar recipes were tested for the different types of lime so that all mortars had the same consistency, a consistency similar to that usually used in bricklaying. Mortars were mixed in accordance with standard EN 1015–2[5]. Preparation and storage of test specimens as well as testing of flexural and compressive strength was performed in accordance with standard EN 1015-11[6]. Prisms measuring 40×40×160 mm were cast, which after seven days were stored in a climate room with a temperature of 20°C and 65% relative humidity. Compressive strength tests were performed with a a Shimadzu AGS-X at five different mortar ages: 1, 3, 6, 12 and 24 months. Carbonated mortar has a lower pH value than mortar that not yet has carbonated, which means that the depth of carbonation could be made visible with a pH indicator applied to a cross-section of the material.

3. Results and discussion

3.1 Compressive strength over time

All mortars except the lime-cement mortar had compressive strengths that increased with age, the lime-cement-mortar reaching a stable state after only 28 days. The compressive strength of the mortars made with traditional Swedish limes increased between 122% and 301% when comparing the measurement after 1 month to the measurement after 24 months. The mortars with industrially produced hydraulic limes increased between 40 and 86% over the same time. The strength after two years of the GT and NHL5 mortars was probably higher than what appeared in the results, which is because the used equipment could not measure greater strength than 6,25 MPa.

3.2 Carbonation

After two years, only four out of twelve mortars were fully carbonated, i.e. 20 mm into the centre of the sample body. The lime-cement mortar was completely carbonated after only 1 month, and after that the strength was stable. Only after 24 months of hardening only three more mortars (ÖT, NHL3,5 and KC) had

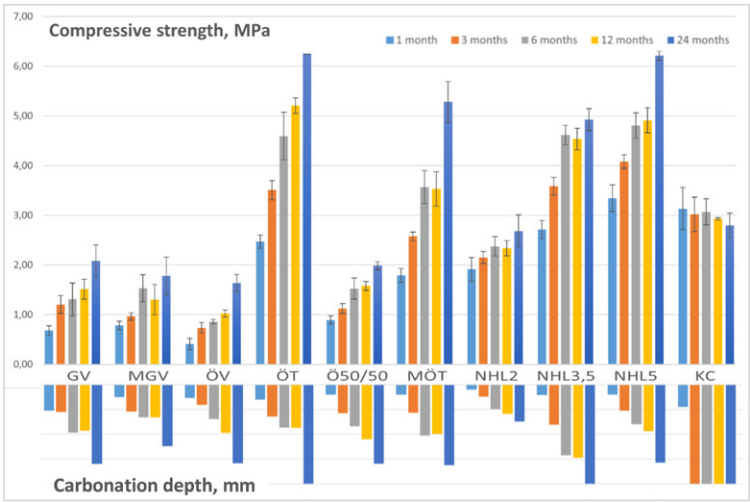

Figure 1 The diagram shows the compressive strength of the mortars at five different ages as well as the carbonation depths.

4 European Committee for Standardization [CEN],1999b.
5 European Committee for Standardization [CEN], 1999a.
6 European Committee for Standardization [CEN], 2019.

carbonated completely. As the study was concluded after two years, it was not possible to determine the strength of these mortars after full carbonation.

4. Conclusions

Time must be a parameter when testing lime. The short perspective, like 28 days, says very little about the final properties of the lime mortar. Some of the hydraulic lime varieties developed a strength that far exceeded lime cement mortar. Material properties should be tested after many years; preferably five or even ten years. It is of great importance to understand this slow increase in strength when choosing a restoration mortar.

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Time to re-evaluate the long-standing use of 1:3 lime mortar for repairs in historic mortar?

1. Introduction

A principal tenet in conservation is to use historically authentic like-for-like replacement materials for repair. This principle is fundamental in regard to built heritage and wall paintings. Differences in material properties between the historic material and the repair material can cause damage to either of the two materials, particularly if they react differently to stresses induced by structural movement or fluctuations in relative humidity, temperature and moisture[1]. If the repairs are stronger than the original, the damage will be to the original. This principle of weaker repairs as well as issues related to the difficulties in producing historically accurate repairs and a practice rooted in the "lime revival" gave rise to the use of standard 1:3 (vol.%) air lime putty mortar for repairs in built heritage and wall paintings, evolving over the years into an ingrained practice[2]. However, one may question whether such a repair mortar, albeit following the principles of being weaker than the historic mortar, could cause harm to lime-rich historic plaster due to differences in microstructure and hygric properties. This issue is examined in the present paper, where pronounced differences in the properties of the highly lime-rich medieval wall painting plaster in Denmark and the 1:3 lime putty repair plaster used in conservation provide an indication that best-practice principles are not being fulfilled, thus posing a challenge for the continuation of a more than 40-year-old Danish practice.

2. Methods

Examining the compatibility of hygric properties between lime-rich medieval plaster and 1:3 lime putty plaster, microstructural comparisons were made of samples of medieval plaster and 1:3 plaster samples using thin-section analyses (PLM), Scanning Electron Microscopy (SEM), measurements of open porosity (DS/EN 772-4:1998) and mercury intrusion porosimetry. Hygric behaviour was studied by examining previously performed water absorption rate measurements[3] and studying migration patterns in replicas of medieval plaster and replicas made from a 1:3 lime putty mortar and a 1:2 hot-mixed mortar. The latter was included as a comparison to provide a material with properties closer to historic plaster than the 1:3 mortar, substantiated by studies supporting the theory that medieval plaster in Danish churches was produced by the hot-mixed method[4]. Since Danish medieval wall painting plaster is limewashed, the role of the limewash on hygric behaviour was also studied. Tests were conducted with poultices loaded with the blue dye Bromophenol Blue to visually assess the water movement through the samples, thereby enabling the measurement of changes in lateral migration over time and the examination of penetration depth and migration patterns in cross sections.

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1 Pender, Ridout, Curteis 2015, 356.
2 Copsey 2019, Midtgaard 2023a.
3 Midtgaard 2023b.
4 Midtgaard 2023a.

3. Results and discussion

The microstructure, porosity and pore size distribution studies showed a significant difference between medieval lime-rich plaster and a 1:3 repair mortar. In optical microscopy, the medieval plaster showed a dense lime matrix with few air entrapments and shrinkage cracks. In contrast, the 1:3 plaster had an open structure, with many air entrapments and shrinkage cracks. Despite this, the medieval plaster showed a higher open porosity than the 1:3 plaster. The higher open porosity is quite possibly caused by the increased number of interconnected micropores in the range 0.1-1 µm, relating to the six times larger volume of lime in medieval plaster (2:1 vol%) and the decreased volume of nonporous aggregates. This increase in capillary active micropores was reflected in the water absorption measurements, showing that the medieval plaster absorbed water 3-4 times faster than the 1:3 plaster. The study also showed that the type of limewash significantly affects the water absorption properties. In the migration studies, in part presented in Figure 1, it was shown that the liquid migrates significantly deeper into a less lime-rich plaster than into a 1:1 hot-mixed plaster. This again reflects the higher volume of capillary pores in the lime-rich plaster, making the lime-rich plaster capable of retaining more liquid per area than the less lime-rich plaster.

Hence, this research indicates that plaster formulations with higher binder-to-aggregate ratios, such as Danish medieval plaster, have a notably more capillary active microstructure than a less lime-rich 1:3 plaster. This suggests that the primary moisture transport pathway in historic plaster repaired with 1:3 mortar would occur outside of the repair (illustrated in Figure 2). Thus, the moisture introduced in the plaster repair process as well as water from rising damp, water ingress, etc. will be primarily transported through the original plaster. This deviates from the intended behaviour of conservation repairs, where the repair mortar should preferentially absorb and dissipate moisture to protect the original fabric[5], especially in scenarios where soluble salts are present within the masonry or wall painting plaster, as the use of 1:3 mortar in such a case might increase the risk of damage in the original wall painting due to efflorescence, subflorescence, and structural weakening.

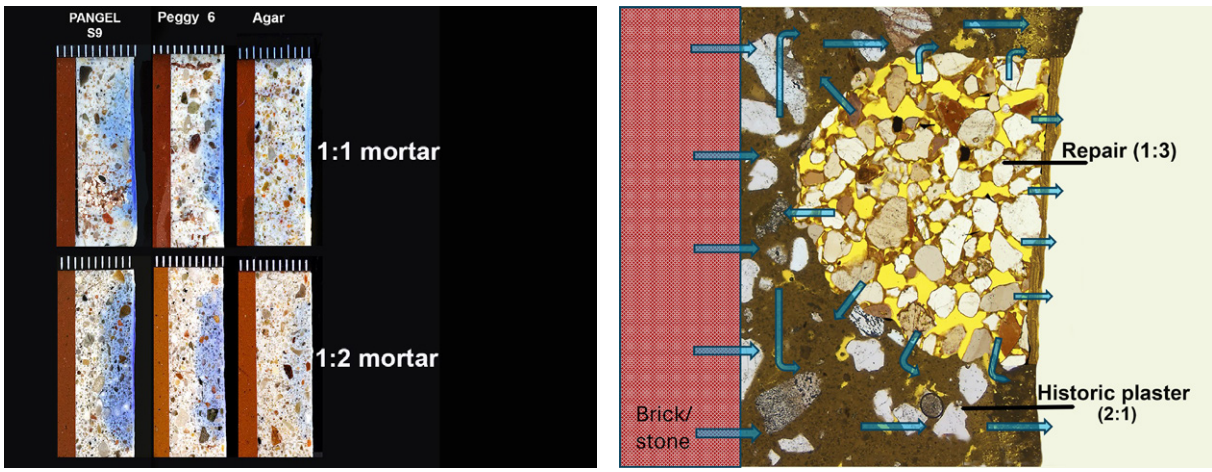

Figure 1. Cross sections of plaster samples subjected to poultices for 180 min, showing how differences in mortar composition change the migration pattern. In the most lime-rich plaster (1:1), the high volume of narrow capillary pores results in a higher concentration of water (blue colour) in the upper part of plaster and limewash

4. Conclusion

The prevailing methodology of employing 1:3 lime putty mortar for the conservation of lime-rich plaster warrants critical re-evaluation, as current findings suggest a fundamental incompatibility with the

5 Válek et al. 2019.

original materials, contravening established conservation principles that advocate for the use of like-for-like materials to ensure compatibility in repairs. The significant differences observed in porosity, microstructure and hygric behavior between 1:3 lime putty mortar and medieval plaster raise serious concerns regarding the long-term integrity and preservation of historic wall paintings. In particular, possibly detrimental moisture dynamics may occur within the composite structure of original plaster and repair mortar, paradoxically instigated by the application of 1:3 mortar that, contrary to intention, may exacerbate deterioration in the original plaster due to lower volume of capillary active pores. Thus, while the principle of utilising repair mortars weaker than the original plaster remains a cornerstone of conservation practice, the assumption that a 1:3 mortar inherently fulfils this requirement without causing unintended consequences necessitates further scrutiny.

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From Historical Mortar Analysis to Natural Hydraulic Lime Revival: A Scientific Pathway for Heritage Conservation in China

1. Introduction

China's masonry heritage, including the Great Wall, the Forbidden City, and the Ancient City of Pingyao, represents critical material evidence of the nation's architectural and cultural evolution. These structures have withstood centuries of environmental and human-induced stresses, reflecting the advanced construction techniques, societal values, and scientific knowledge of ancient China. However, their preservation is threatened by ongoing environmental erosion, including temperature fluctuations, freeze-thaw cycles, and salt crystallization, as well as human impacts like improper restoration. These factors lead to surface weathering, mortar detachment, and structural instability, necessitating urgent conservation efforts[1]. Traditional restoration techniques predominantly use air lime, which, while effective historically, faces significant limitations in modern conservation due to its low early strength, poor water resistance, and high shrinkage[2-3]. As a result, restoration efforts often fall short, requiring frequent maintenance. In contrast, Natural Hydraulic Lime (NHL) has demonstrated success in Europe for its favorable mechanical properties, water resistance, and compatibility with historical materials[4-5]. However, its performance and applicability in China's specific environmental conditions remain underexplored. This study analyzes the properties of historical mortar from the Ming Great Wall and evaluates the compatibility of NHL2 with these mortars, aiming to provide an improved solution for the conservation of China's masonry heritage.

2. Sampling and Testing Methods

The study focused on ancient mortar samples collected from four representative locations in the Dazhuangke section of the Ming Great Wall (as shown in Figure 1). The mechanical properties of the mortar, including compressive strength (the compressive strength of the original mortar was determined using Wang's method[6]), bond strength, and water absorption, were tested. Furthermore, X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric–differential thermal analysis (TG-DTA), and mercury intrusion porosimetry (MIP) were used to analyze the mineralogical composition, chemical constituents, and microstructure of the mortar. To evaluate the compatibility of NHL2, produced by Hessler Kalkwerke (lime-to-sand ratio of 1:3, water-to-lime ratio of 0.6), mortar samples and pure paste specimens were prepared. The mortar specimens were tested for compressive strength, water absorption, and bond strength with Great Wall bricks, while pure paste specimens were analyzed at different curing ages to assess microstructural changes and compatibility with historical materials.

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1 Chen et al. 2024.
2 Aggelakopoulou et al. 2011.
3 Sepulcre-Aguilar et al. 2010.
4 Bras et al. 2010.
5 Baltazar et al. 2014.
6 Wang et al. 2020.

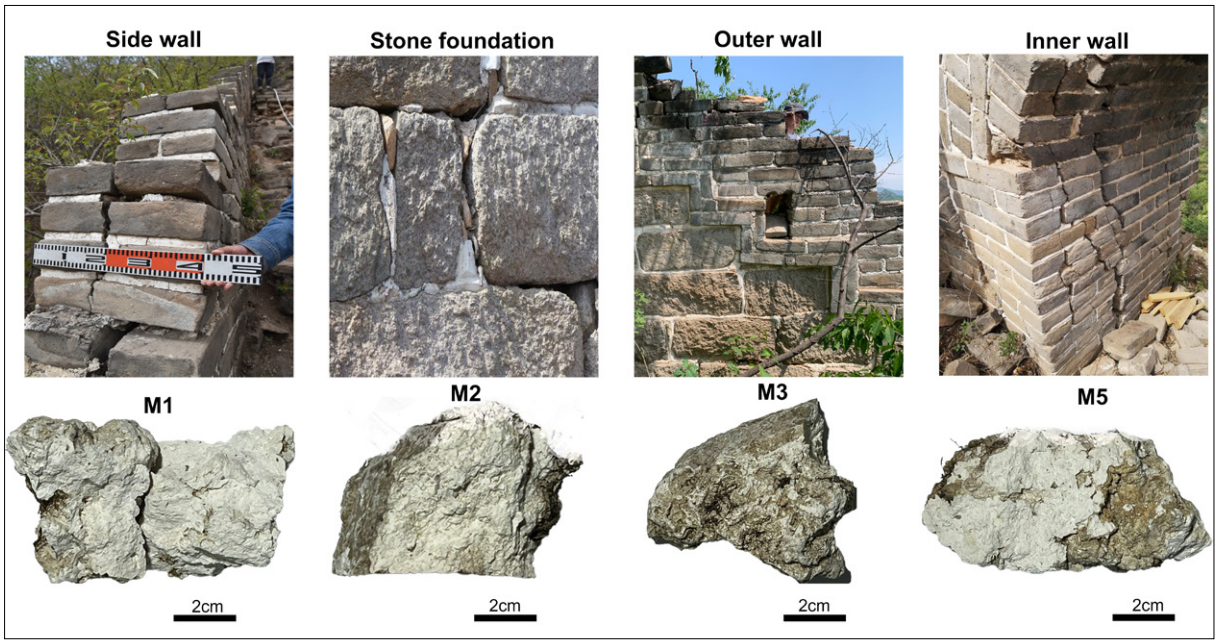

Figure 1. Sampling location diagram.

3. Results and discussion

The compressive strength of the traditional mortar samples ranged from 0.77 to 2.67 MPa, with an average value of 1.62 MPa. The bond strength varied between 0.03 and 0.07 MPa, averaging 0.055 MPa, while the saturated water absorption ranged from 40% to 45%. In comparison, NHL2 specimens after 28 days exhibited a compressive strength of 2.36 MPa, a bond strength of 0.09 MPa, and a saturated water absorption rate of 13%. These results indicate that NHL2 provides comparable mechanical performance to historical mortar while offering significantly improved water resistance. XRF analysis revealed that the historical mortar samples were primarily composed of pure lime, with CaO content exceeding 80%, along with minor amounts of MgO, SiO_2, Al2O_3, and Fe2O_3. XRD analysis further confirmed that all historical mortar samples exhibited a distinct calcite (CaCO3) peak at 2θ≈30°. Additionally, small amounts of magnesite ($MgCO_3$) were detected in samples M1 and M2, suggesting the presence of a minor dolomitic component. TG-DTA analysis showed significant mass loss between 600 and 800 °C, corresponding to the decomposition of $CaCO_3$. The calculated $CaCO_3$ content ranged from 67.05% to 82.24%. In samples M1 and M2, a small endothermic peak was observed between 450 and 550 °C, indicative of $MgCO_3$ decomposition, with estimated $MgCO_3$ contents of 14.39% and 16.32%, respectively. In contrast, samples M3 and M4 had lower $MgCO_3$ contents of 2.78% and 5.37%. MIP testing showed that the pore structure of M1, M3, and M4 mortar samples was predominantly characterized by pores around 1 μm in diameter, whereas M2 mortar exhibited a finer pore structure, with pores concentrated around 0.1 μm. The overall porosity of the historical mortar samples ranged from 33.60% to 46.99%. These findings suggest that the historical mortars, after long-term carbonation, developed a microstructure characteristic of hydraulic lime mortars, with gradual pore densification contributing to improved weathering resistance.

For NHL2, XRD and TG-DTA analyses revealed that its main phases are Ca(OH)2, CaCO3, and minor amounts of calcium-silicate-hydrate (C-S-H) gel, indicating good chemical compatibility with historical mortar. MIP analysis showed a total porosity of 48.06%, with about 50% of pores larger than 1000 nm, supporting breathability in masonry structures. As the final compressive strength of NHL2 may exceed 5 MPa, the binder-to-sand ratio should be carefully controlled to ensure balanced strength development. These characteristics make NHL2 a promising material for restoring the Ming Dynasty Great Wall.

4. Conclusions

This study systematically analyzed historical mortar samples from the Ming Dynasty Great Wall and compared their properties with natural hydraulic lime (NHL2) to evaluate its suitability for conservation and restoration purposes. The results showed that traditional mortars exhibited moderate mechanical strength, high porosity, and significant $CaCO_3$ content, which are characteristic of pure lime-based materials. NHL2 demonstrated comparable mechanical performance, improved water resistance, and similar microstructural characteristics, including compatible mineralogical composition and appropriate porosity. These findings suggest that NHL2 is a promising alternative to traditional air lime mortars for the conservation and restoration of masonry heritage structures in China.

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Abstract

This study examines the properties of ancient mortar from the Ming Dynasty Great Wall and compares them with natural hydraulic lime (NHL2) for restoration purposes. Mechanical properties, including compressive strength, bond strength, and water absorption, were tested, along with XRF, XRD, TG-DTA, and MIP analyses to assess the mineral composition and porosity of the historical mortar. The results show that the compressive strength (2.36 MPa) and bond strength (0.09 MPa) of NHL2 are similar to those of the historical mortar, while its water absorption (13%) is significantly lower than that of the historical mortar (40%~45%). The mineral composition of NHL2 is highly compatible with the historical mortar, indicating its potential as a suitable material for the conservation and restoration of China's masonry heritage.

Key words

Ming Great Wall, natural hydraulic lime, mechanical properties, compatibility

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Novel techniques for the assessment of injectability and environmental resistance of injection grouts for mosaic conservation

1. Extended abstract

Over the past two decades, numerous commercial injection grouts have emerged in the market, becoming popular choices among conservators worldwide for the restoration and stabilization of architectural surfaces[1]. These grouts offer a convenient alternative to custom formulations. However, specific standardized test methods to evaluate injectability, flowability, and resistance to saline attack for this class of products during the conservation of plasters, wall paintings, and mosaics remain undeveloped.

This study characterized five commercially available injection grouts by adapting the sand column test (EN 1771) to assess the grouts' ability to fill capillary networks within various granular materials, in both dry and pre-wetted states, under constant pressure conditions[2].Concurrently, a systematic rheometric characterization of the grouts was performed at different water-to-solid ratios.

Mineralogical analysis through X-ray Powder Diffraction (XRPD) and Fourier-Transform Infrared Spectroscopy (FTIR) revealed that the grouts are composed of a binder and a filler. The filler, either limestone or silica, represents slightly more than 50 wt% in all grouts except Ledan TB1, where it comprises approximately 75 wt%. The binder is based on Portland cement in most grouts, except in PLM-1 and Bio Aedilitia where it is based on NHL (Natural Hydraulic Lime). All materials follow the requirementsfor grouth consolidation[3].

Regarding particle size distribution, Ledan products exhibit a principal mode centered at approximately 3 μm, while all others display a principal mode centered at approximately 20 μm. This difference significantly influences fluidity: Ledan grouts are less fluid, exhibit higher yield stress, and have greater water demand, but consequently demonstrate enhanced stability against sedimentation.

Mechanical strength correlates with the nature of the binder: grouts showing higher C3S/C2S values and likely containing a cement-based binder exhibit the highest mechanical strength[4]. However, these grouts demonstrate the lowest resistance to sulfate attack, while those with low C3S/C2S values and likely containing an NHL binder show the highest sulfate resistance[5].

Optimization of grout fluidity, achieved by selecting the optimum water-to-solid ratio, improves stability against sedimentation[6] but does not enhance overall injectability[7]. It is not possible to control viscosity at both low (for sedimentation) and high (for injection) shear rates by modifying the water-to-solid ratio alone. Moreover, the high water absorption of crushed brick may necessitate additional water.

The key to achieving good injectability in a grout lies in its cohesivity, which can be controlled by selecting the appropriate particle size distribution or potentially through the addition of rheology modifiers. Sulfate

1 Ferragni et al. 1984, 110-116.
2 Biçer-Simsir, Rainer 2011.
3 Valluzzi 2009, 382-397; Baglioni et al. 1997, 43-54.
4 Miltiadou-Fezans, Tassios 2022.
5 Griffin 2004, 23-34.
6 Miltiadou-Fezans, Tassios 2013.
7 Jorne, Henriques 2016.

resistance is obtained through the proper selection of binder, with NHL performing better than cement in this regard.

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Enhancing Air Lime Mortars with Slag: Mechanistic Insights into Reaction Kinetics, Strength Development, and CO2 Mineralization Optimization

1. Background of the work

Extended setting time, strength gain and poor workability are responsible for the reduced use of air lime in the construction sector[1]. To improve the setting and strength properties, the use of mineral admixtures is imperative to develop it as compatible materials for heritage preservation[2]. Ground Granulated Blast Furnace Slag (GGBS) is an industrial residue that is a globally accepted pozzolan. The additive can reduce the water demand, setting time and increase the mechanical properties. Optimising a hydration level before carbonation is imperative to overcome the slow setting and strength gain challenge. However having a higher level of hydration precipitates higher quantum of hydration products that densifies the system. Therefore, choosing the right additive is important in a lime based system. The addition of GGBS in proportions of 10, 20, 30, 40 and 50% by weight of binder is tried in air lime binders, while monitoring the compatibility criterion. An optimised ready mix mixture is proposed in the current work that can be used as repair grout and as a commercial mortar/plaster for commercial applications. As carbonation is the predominant reaction that occurs in a lime based system, the mortar can be optimised as a CO2 sink. Any mineral admixture added will release hydration products, however further carbonates. Therefore, the effect of further carbonation is also looked into. The developed binder is therefore checked for its compatibility, reaction evolution- considering the initial hydraulic reactions and further carbonation and CO2 uptake.

2. Materials and methods

Air lime with 99% purity was used as the main ingredient. GGBS was procured from JSW Steel Industry, Mumbai, India. The specific gravity of the material was measured as 2.9. Crushed sand was used as the aggregate, maintaining a binder-to-aggregate ratio of 1:3. GGBS was added in air lime mortars with replacement levels of 10 to 50%, designated as S10 for 10% GGBS, S20, S30, S40 and S50. Water content in the system was fixed with flow table test according to IS 5512 (1983), which gives the output in terms of flow diameter. The amount of water that gave a flow table diameter of around 180 mm was fixed as the water-to-binder ratio. Setting time was determined according to ASTM C807. The mortar after flow test was cast in 50×50 mm sized cubes and subjected to air curing (natural carbonation) for 28 days.

3. Results and discussions

The section briefs on the results of setting time and compressive strength of various mortar mixtures. Figure 1 (a) illustrates the penetration depth versus time data that indicates the initial and final setting times of modified mortars. The figure particularly shows the data of pure air lime mortar and mortar with 40% GGBS in lime. The final setting of pure air lime extended for hours and was unable to capture

1 Ergenc et al. 2018.
2 Loureiro et al. 2020.

in automatic Vicat. The final setting of air lime generally occurs after 3 days of curing. With addition of 40% GGBS, the final setting time was shortened to 200 minutes. Hence, the mineral admixture chosen is capable to reduce setting time significantly. Figure 1 (b) shows the 3, 7 and 28-day compressive strength of modified mortars. As anticipated with increase in GGBS content, the compressive strength increased. The initial hydraulic reactions are responsible for the higher compressive strength. Detailed studies on compatibility criterion, water transport and vapour movement are required to optimise GGBS content in air lime binders that are ongoing in the laboratory.

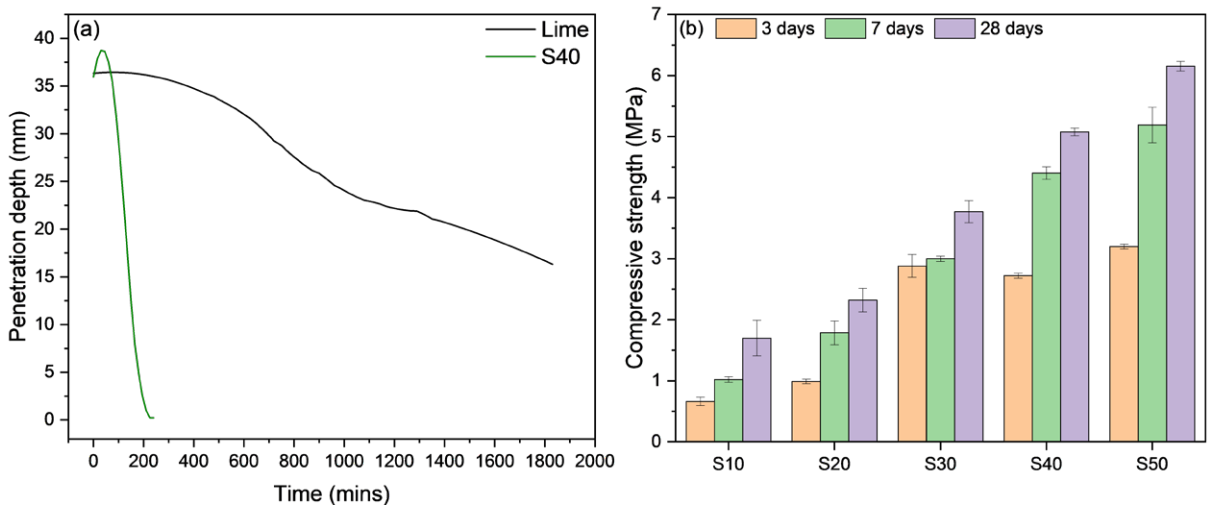

Figure 1. (a) Setting time variation for modified mixtures, (b) Compressive strength of modified mixtures

4. Conclusions

Addition of mineral admixtures in air lime mortars is important to overcome the slow setting and strength gain challenges and for efficient application in heritage and commercial sites. The work is detailed study on incorporating GGBS to lime mortars; analyzing their compatibility, mechanical properties and reaction mechanisms, out of which a brief glimpse is presented here. GGBS has the potential to reduce water demand, reduce setting time and increase the compressive strength of air lime mortars, while maintaining compatibility with heritage materials. The effect of further carbonation on CO2 uptake, physical, mechanical and microstructural properties is also focused in the paper.

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Red Mud Mortars: A Sustainable Solution for the Restoration of Contemporary Buildings

1. Introduction – Background and objective of the study

This study delves into the use of red mud-derived mortars as an innovative approach to restoring contemporary edifices, balancing aesthetic considerations with functional benefits. By leveraging the distinctive colour and texture imparted by red mud, the investigated mortars can be tailored to closely match the appearance of traditional building materials such as red brick or sandstone. This makes them particularly suitable for repairs on modern architecture buildings and constructions from the last two centuries that require careful restoration. Red mud, a highly alkaline by-product generated during of alumina production, poses a major presents significant environmental challenge owingchallenges due to its highly alkaline nature and the substantial quantities produced. Nonetheless, this industrial waste holds significant potential for utilization large volume. However, its use in the construction sector across various applications, such as the development of low-carbon cementitious materials and environmental remediation efforts. Incorporating red mud, particularly as a partial cement replacement for cement not only minimizes the, can reduce reliance on conventionaltraditional raw materials like limestone and clay but also aids in preserving, conserve natural resources and mitigating the ecological impacts of mining activities. Furthermore, its use contributes to, and lower the industry's carbon footprint. This approach not only promotes waste reduction and offers an opportunity to lower the but also supports more sustainable construction industry's overall carbon footprint, addressing multiple environmental concerns simultaneously.practices. Red mud in two forms viz., both oven -dried and incinerated at 300°C were, was used to prepare cementitious mortars replacing cement partially up to replace cement in mortars at levels of 5%, 10%, and 15% by weight at increment of 5%. Red mud powders were evaluated for pozzolanic activity and photocatalytic activity for environmental pollutant gas removal.. The mortarscementitious materials incorporating red mud were evaluated for strength and hydration kinetics at early-stage of hydration. Red mud powders were investigated for their photocatalytic activity in removing environmental pollutant gases, revealing a novel application beyond their conventional use in construction. The study demonstratedshowed that mortars incorporating red mud powders exhibit higher efficacy in not only meet structural requirements but could also offer enhanced air purification capabilities, particularly inthrough the effective reduction of nitrogen oxide concentrations. The investigated mortars can be utilized to match the appearance of red brick or sandstone, making them suitable for repairs on modern architecture buildings and constructions from the last two centuries that require careful restoration. This dual functionality positions red mud-based mortars as innovative materials that contribute to both the structural integrity and environmental remediation of built environments.

2. Experimental programme – Materials and Methods

A reference mix is prepared using a conventional 1:3 cement-to-sand ratio by weight. Table 1 displays the chemical composition of the binding materials utilized in this study, CEMIII42.5 SR and red mud that has been oven-dried and incinerated at 300°C. For the preparation of seven mortar samples listed in Table 2, CEN standard sand was employed.

The modified Chapelle test was employed to assess the pozzolanic activity of red mud powders, while their photocatalytic activity was evaluated using the nitrogen oxide (NO) abatement test. A photoreactor supplied with 0.78 L min−1 of 500 ppb NO in air was used for NO abatement test. Following a 30-minute equilibration, samples were exposed to a 300 W Ultravitalux lamp for one hour. The use of an ultraviolet filter that eliminated this fraction of the spectrum made it possible to study the samples under solar irradiation (UV + visible light) and under strict visible irradiation. Isothermal calorimeter was utilized to investigate the hydration kinetics, with heat flow curves providing insights into the process. The mechanical performance of the mortars was evaluated by measuring their compressive strength at both 7 and 28 days of curing complying with BS EN 1015-11:2019[1].

3. Results and discussion

Red mud powders exhibited photocatalytic capabilities, as evidenced by their partial degradation of NO – Table 1. This property may be attributed to the presence of hematite, which was identified in the chemical composition analysis. The demonstrated ability of red mud to break down pollutants suggests its capacity for environmental remediation and pollution control. At lower substitution levels, the 7-day compressive strength of mortars containing RM300 exhibits comparable performance to their respective RM105 counterparts. Notably, the variation in 7-day compressive strength among mixes R5-300, R10-300, R5-105, and R10-105 deviates less than 5% from the mean. Furthermore, red mud-based mortars with 5% and 10% substitution rates demonstrate no significant difference in compressive strength compared to the reference mix. At the 15% substitution level, R15-300 shows a marginal improvement (9%) over R15-105; however, both mortars exhibit reduced compressive strength relative to the reference mix. Incinerating red mud to 300°C has not contributed to strength improvement as evident from the reduced compressive strength values of RM300-based mortars in comparison to the reference mix. Red mud powder is not pozzolanic as evident from the modified Chapelle test observations. The minimum amount of Ca(OH)2 fixed by a material should be 650 mg/g to consider it has pozzolanic reactivity[2].

The dilution effect of cement and the reduced pozzolanic activity of red mud might have led to a relatively more porous microstructure thus impacting strength development at 28 days. The hydration mechanism of red mud is intricate. Both RM-105 and RM-300 exhibit alkalinity with pH values of 11.5 and 11.2, respectively. Its high alkalinity and fine particle size enhance hydration by serving as a filler and offering nucleation sites. Nevertheless, its limited capacity to fill pores resulting from cement dilution, combined with its absence of pozzolanic activity, adversely affects the 28-day compressive strength. Red mud-based mortars remain viable for certain repair applications, contingent on specific strength and functional needs. Figure 1 shows a typical red mud-based mortar sample under compression.

Red mud incorporation lowers peak and cumulative hydration heat and delays peak hydration time (Table 2). The third heat flow peak, linked to aluminate phases reacting with ettringite to form mono-sulfoaluminate/hydroxy-AFm after gypsum depletion, is notably influenced by red mud content. Higher red mud concentrations intensify and accelerate this peak, likely due to its aluminum-rich composition. During the deceleration stage, the third (aluminate) peak corresponds to monosulphate (AFm) formation, driven by sulfate desorption from C-S-H, rapid C3A dissolution, and ettringite precipitation. Hydration slowdown arises from thickened hydration product layers around cement particles, which impede water diffusion to unreacted cores. This diffusion-controlled regime inversely correlates hydration rate with layer thickness.

3. Conclusion

The dual potential of red mud is noteworthy: it demonstrates efficacy in mitigating environmental contamination while simultaneously offering promise as a sustainable repair mortar for modern structures. This industrial byproduct's versatility presents an opportunity to address both ecological concerns and construction material needs in contemporary building practices.

1 BS EN 1015-11:2019.
2 Liu et al. 2023.

Chemical composition				Photocatalytic activity test		NO abatement test	
Main metal oxides	CEMIII	RM-105	RM-300	Sample	CaO consumption/g pozzolan material (mg)	Percentage abatement (%)	
						NO	NOx
CaO	58.39	3.44	3.43	RM-105	514	10.4	4.8
MgO	3.81	0.34	0.44	RM-300	498	9.1	8
Al_2O_3	7.47	16.33	16.1	RM-105-F*	-	4.8	4.8
SiO_2	21.22	7.01	6.81	RM-300-F*	-	4.8	4.6
Fe_2O_3	2.58	58.94	59.88		-	-	-
SO_3	4.25	0.49	0.5		-	-	-
Na_2O	-	3.71	3.94		-	-	-
TiO_2	0.50	8.30	7.61		-	-	
*NO and NOx percentage abatement values for samples with abbreviation with letter 'F' at end indicates these samples are tested under strict visible light irradiation.							

Table 1. Chemical composition of the raw materials. Pozzolanic activity and nitrogen oxide abatement test for red mud powders

Sample	Compressive St (MPa)		Arrival time of prominent exothermic peak (in hrs:min:sec)	Normalised heat flow corresponding to prominent exothermic peak (mW/g)	Cumulative heat released at 72 h (J/g)
	7-day	28-day			
Reference	21.56	37.00	8:52:07	273,899	238.22
R5-105	22.41	37.38	10:23:15	135,921	164.42
R10-105	20.30	29.80	19:28:03	169,567	179.79
R15-105	16.54	20.59	14:56:08	189,263	161.93
R5-300	21.29	32.19	9:50:01	169,243	179.27
R10-300	21.31	31.78	10:20:07	122,216	153.34
R15-300	18.07	25.78	15:54:01	197,511	166.79
Typical nomenclature for mortar is represented as RX-Y, where 'X' represents replacement levels of cement with RM (5, 10 or 15), and 'Y' represents the treated temperature (either 105°C or 300°C).					

Table 2. Strength development and isothermal calorimetry results of mortars

Figure 1 Red mud mortar in compression.

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Natural wollastonite as a performance enhancer for lime mortars

1. Introduction

The performance of air lime mortars can be improved by adding various types of additives and admixtures. The most common for this purpose are substances with pozzolanic or hydraulic properties. The addition of various types of fibers, whether natural (plant or animal) or synthetic, can be used to improve the resistance of lime mortars to the formation of drying shrinkage cracks and increase the flexural strength. Wollastonite belongs to the group of natural microfibers, it is an acicular, white mineral with the chemical composition β-CaSiO3. It is usually completely crystalline, without pozzolanic activity. It is mainly used in ceramics, friction products, paint fillers and plastics. Research into its use in the construction industry has focused mainly on its use in cement composites and alkali-activated materials, where its positive effect has been confirmed in accelerating the hydration process[1], reducing the formation of shrinkage cracks and improving flexural strength, while slightly reducing compressive strength[2-3]. The use of wollastonite in lime mortars has not yet been published.

2. Materials and methods

Hydrated lime CL90-S according to EN 459-1 with a maximum particle size of 30 μm and a, specific gravity of 2.42 g cm−3, and specific surface area 141901420 m2 kg−1 was used as a binder in the prepared mortar mixes. Pure quartz sand complying with EN 13139 (0/2 mm fraction) was used as the aggregate, and fine natural wollastonite with a maximum particle size of 0.5 mm, specific gravity 2.85 g cm−3, and specific surface area 3430340 m2 kg−1 was added to the mixtures as a partial lime substitute at 0%, 5%, 10%, 15%, 20%, 25% and 30% by weight. Mortar mixes were prepared using a constant volume ratio of binder (lime + wollastonite) to aggregate of 1:1 and the same amount of water to achieve a similar workability of 160 ± 5 mm according to EN 1015-3 (Table 1). The specimens (40 mm × 40 mm × 160 mm) were demoulded after 48 hours and cured for 26 days under laboratory conditions at T = (22 ±3) °C, RH = (45 ±5) %.

Water retention value (WRV), bulk density (ρfm), and entrained air in fresh mortars were set according to EN 459–2. Bulk density of hardened mortars, flexural strength and compressive strength were determined according to EN 1015-10 and EN 1015-11. High-pressure mercury intrusion porosimetry (MIP) was used to investigate the pore structures of the samples including the determination of total open porosity (TOP) and pore size distribution. The water absorption (Aw) of the sample by immersion at atmospheric pressure was evaluated according to EN 13755.

1 Khan, Ashraf 2019.
2 Low, Beaudoin 1994.
3 Abdel Wahab et al. 2017.

Mixture	Lime (g)	Wollastonite (g)	Quartz sand (g)	H2O (ml)	Flow (mm)	ρm (kg m-3)	Air content (%)	WRV (%)
L-ref	100	–	355	105	155	1864	5,2	96,03
LW-5	95	5	356		165	1881	4,8	91,50
LW-10	90	10	358		161	1873	4,7	91,68
LW-15	85	15	359		163	1895	4,2	91,7
LW-20	80	20	360		162	1851	5,3	91,52
LW-25	75	25	361		157	1862	5,2	93,72
LW-30	70	30	362		155	1822	6,2	92,53

Table 1. Composition and fresh state properties of mortar mixtures

3. Results and discussion

As can be seen from Table 1, there was a good correlation between the bulk density of the fresh mortars and the air content in the mortars. The airiest mortar (LW-30) had the lowest bulk density and vice versa (LW-15). All mortars with wollastonite had poorer water retention than the reference mortar, although this ability increased with increasing wollastonite dosage. The bulk density of the hardened mortars was primarily affected by their total open porosity (Figure 1). The bulk density of the mortars containing wollastonite decreased slightly due to a small excess of mixing water (see flow values in Table 1). All mortars with wollastonite showed higher flexural and compressive strengths than the reference mortar (Figure 1). With increasing wollastonite content in the mortar, the strengths gradually increased (LW-30 achieved 70% higher flexural strength and 40% higher compressive strength than L-ref). The effect of added wollastonite was therefore different from the effect on the properties of cement mortars. Partial replacement of very fine lime with coarser wollastonite results in an increase in strength - wollastonite does not act as a filler here due to its particle size but still increases strength. Such a significant increase in strength was surprising as wollastonite didn't show any pozzolanic activity (26 mg (Ca(OH)2/1 g; according to the Chapelle test).

The total open porosity of the mortars increased slightly after partial replacement of lime with wollastonite due to the greater coarseness of wollastonite, while the water absorption of the mortars at atmospheric pressure (Figure 1) decreased slightly. Porosimetric measurements also show that mortars with wollastonite contained fewer large pores with a diameter of more than 15 µm and fewer small capillary pores with a size of less than 0.15 µm. Replacing lime with wollastonite reduced the size range of the most common pores in mortars. Small capillary pores around 0.25 µm in diameter were similarly represented in mortars, while the representation of wider pores around 3 µm and 10 µm in diameter increased with increasing wollastonite content.

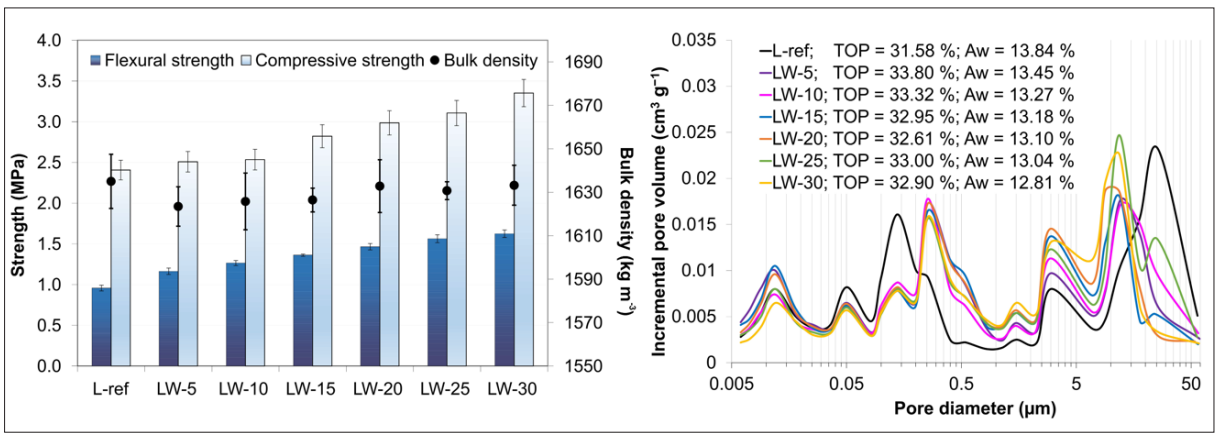

Figure 1. Mechanical properties and structural parameters of mortars after 28 days (TOP – total open porosity; Aw – water absorption)

4. Conclusions

Based on preliminary research findings, natural wollastonite of high purity serves as an effective performance enhancer for lime mortars. It notably improves both flexural and compressive strength, despite causing a very slight reduction in bulk density. Additionally, it slightly decreases water absorption while increasing total open porosity, suggesting that the mortars likely retain their beneficial diffusion properties—though further verification is required. Given these characteristics, natural wollastonite shows strong potential for application in lime mortars. Unlike cement mortars, it does not reduce their compressive strength and, due to its structure, acts as a micro-reinforcement. The detailed behaviour of wollastonite in lime mortars including the resistance and durability of lime-wollastonite mortars, and as well as the microstructure of the mortars and their transport properties (capillary suction, water vapor diffusion or heat transport) are the subject of ongoing research. An undeniable advantage of these mortars is their lower carbon footprint compared to pure air lime or natural hydraulic lime mortars.

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Mineralogy of lime pastes with metakaolin and construction and demolition waste for application in restoration works of historic buildings

1. Introduction

The imminent environmental impacts predicted for the coming decades require a significant reformulation in construction practices, because the construction industry is currently responsible for around 8% of global CO2 emissions and for generating 25% to 30% of solid waste worldwide. In this context, it is urgent to seek more sustainable alternatives for the materials used in civil construction, which includes the restoration of historic buildings[1-2].

Traditionally, before the popularization of Portland cement, lime, combined with pozzolans, was the main binder used in constructions[3]. Nowadays, to restore these historic works, it is essential that the materials used are compatible with the originals used at the time of construction, otherwise the structures are susceptible to pathological manifestations[4-5-6]. Previous studies[7-8], indicated that many historic constructions were built with mixtures of hydrated lime and materials from different sources, with allow us to infer that replacing part of these materials with construction and demolition waste (CDW) may be viable, as long as it does not compromise the compatibility of the pastes or mortars used in the interventions.

Thus, the purpose of this article is to analyze the mineralogy of pastes formed by a ternary mixture of hydrated lime, metakaolin (MK) and construction and demolition waste and compare them with a reference paste (lime with metakaolin) in order to identify whether the insertion of CDW up to a certain percentage can be used in the restoration of historic buildings. This research aims to contribute to the mitigation of environmental impacts caused by civil construction through the promotion of sustainable alternatives for the preservation of historical heritage.

2. Materials (mixtures) and methods

2.1 Mixtures

After carrying out workability tests with different water/binder ratios and with replacement, by mass, of different lime contents with metakaolin by CDW, the reference mixture was defined (50% lime and 50% MK) and three mixtures with CDW, whose replacement was of 10 in 10% up to a maximum of 30%. The water/binder ratio chosen for all mixtures was 0.8[9] Subsequently, the characterization of the mixtures in

1 Gartner, Hirao 2015.
2 Robayo-Salazar, Valencia-Saavedra, Gutiérrez 2020.
3 Velosa 2006.
4 Cincotto, Quarcioni, John 2007.
5 Magalhães 2018.
6 Souza 2019.
7 Arcolao 1998.
8 Santiago 2012.
9 Siqueira Júnior, Nóbrega, Carneiro 2022.

the anhydrous state was carried out. The specific mass of the mixtures was: reference - 2.45g/cm^3; 10% CDW – 2.45g/cm^3; 20% CDW – 2.47g/cm^3; 30% CDW – 2.49g/cm^3.

2.2 Methods

For the comparative evaluation of the compatibility between the pastes with CDW and the reference one, the following tests were performed at 14, 28, 56 and 90 days of curing: X-ray diffraction (XRD); thermogravimetry (TGA) and differential thermal analysis (DTA).

3. Summary of results

3.1 X-ray diffraction (90 days)

After 90 days of curing, it was found that a greater replacement of lime with metakaolin by CDW reduces the amount of calcium carbonate phases (calcite and aragonite), which are essential for the formation of a more cohesive and resistant matrix. The presence of a large amount of biotite in samples from 20% of CDW suggests that the residue contains minerals that do not react significantly with lime, which results in a more fragile structure.

3.2 DTA-TGA (90 days)

The DTA-TGA at 90 days shows that, compared to the test carried out at 56 days, the carbonation process was intense in this period (from the 56th to the 90th day), in which it is clear that fewer pozzolanic reactions occurred. The greater decarbonation presented by the reference paste is justified by the fact that it is the mixture with the greatest availability of Ca(OH)2 to react with CO2 throughout the analyzed period. Consequently, thanks to the higher CaCO3 content formed between 56th and 90th days, it became the one that presented the highest decarbonation at 90 days. As in the XRDs, the DTA-TGA tests also indicate that the pastes containing 10% CDW and the reference are compatible.

4. Conclusions

Among the mixtures made, the one containing 10% CDW mass replacement stands out as the most promising to be used in restoration works, as the results obtained in the tests do not differ significantly from each other (reference and 10%). These results suggest that the use of CDW in small proportions can be a viable and effective alternative for the preservation of historical heritage, without compromising the compatibility of the original materials, avoiding the emergence of pathological manifestations in the building.

X-ray diffraction analysis combined with thermogravimetry and differential thermal analysis tests indicated that even with the insertion of up to 10% of CDW, the characteristics of the pastes were not drastically altered, demonstrating the viability of using this residue in the composition of restoration materials. However, replacing CDW in a greater proportion (20% or more) compromises the compatibility of the material, mainly due to the presence of minerals such as biotite that do not react with lime, weakening the paste matrix.

Future investigations, which vary the types of inputs used (different limes, metakaolins and CDWs) and employ different curing conditions (temperature, humidity and time) in the mixtures will be essential for understanding the behaviour and structure of the new material formed, in order to offer new perspectives for optimizing the use of these materials in the preservation of historical heritage. Additionally, a life cycle analysis is necessary to assess whether the energy comsuption involved in using CDW as a binder is more advantageous than that of producing lime or metakaolin.

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Natural mineral rheology modifiers for lime-based grouts

1. Introduction

Injection grouting is a technique used in repairs of masonry and plasterwork of heritage structures. The grouting is irreversible therefore during a design period much attention is given to the compatibility of the grouts with the surrounding materials[1]. For this reason, lime based grouts are preferred in the practice. The properties of injecting grouts are modified by various additives, the two most frequently used being pozzolanic additives to aid the strength development especially in the applications with limited air access and rheology modifiers responsible for good injectability, fluidity, and limited segregation. The most commonly used rheology modifiers are cellulose ethers used to increase viscosity and water retention, mitigating bleeding and segregation, and plasticisers/water reducers to improve fluidity and injectability while reducing the amount of water to values ensuring improved strength and durability[2]. The work studies the effect of natural rheology modifiers on the rheology of lime based grouts. The modifiers used are attapulgite (palygorskite), montmorillonite, sepiolite, and wollastonite; three clay minerals and calcium inosilicate. These minerals affect rheology mainly though their fibrous structure, increasing thixotropy of the solution, improving suspension stability, and increasing yield stress and plastic viscosity[3-4-5-6-7].

2. Materials and methods

The grouts with 2, 4, 6, 8, and 10 vol.% of CL 90 S lime replaced by mineral additive were prepared (using precise weight ratios calculated based on loose bulk densities presented in Table 1) with water/solid (w/s) ratio (Figure 1) modified to achieve, after 60 s of intensive mixing, the pre-defined mini-slump value corresponding to 250 mm spread using cone compliant with EN 1015-3. The measuring procedure using TA Discovery HR1 hybrid rheometer consisted of 60 s of preshear at 50 s-1, followed by 60 s resting period and 0 s-1 to 100 s-1 to 0 s-1 flow sweep test; after 105 s of resting period the amplitude sweep test at 10 rad s-1 angular frequency and strain from 0,001% to 10% was conducted. The downcurves from flow properties were studied using Bingham model ($\tau=\tau_0+\eta\dot{\gamma}$; where τ_0 is yield stress, η is plastic viscosity, and $\dot{\gamma}$ is strain) while the length of linear viscoelastic region, value of storage modulus in this region and flow point were main concerns of amplitude sweep test.

1 Papayianni et al. 2023.
2 Bicer-Simsir et al. 2010.
3 Liu, et al. 2023.
4 Chunran, Shicong 2018.
5 Benyounes 2019.
6 Yücel et al. 2023.
7 Zhao et al. 2025.

	Abbreviation	Loose bulk density (kg m^{-3})	Specific surface area (m^2 kg^{-1})	d10 (µm)	d50 (µm)	d90 (µm)
Lime	L	470	2065	0.49	2.66	182.16
Montmorillonite	Mon	858	225	7.54	31.11	68.82
Sepiolite	Sep	141	3735	4.92	12.17	30.67
Attapulgite	Att	453	876	7.27	37.62	94.42
Wollastonite	Wol	407	343	8.71	41.30	111.65

Table 1. Properties of dry raw materials.

3. Results and discussion

3.1 Flow properties

The water/solid ratio (w/s; Figure 1) decreased with increasing percentage of lime replaced by natural rheology modifiers, except for sepiolite at higher doses due to its significantly higher specific surface area and finer granulometry (Table 1) compared to other additives. The yield stress was slightly increased when lime was replaced by a rheology modifier, with the highest increase in the case of sepiolite and the lowest differences in the case of montmorillonite. This increase would lead to the higher initial resistance of modified grout to the external force causing the flow and its lower ability to fill up voids; an undesirable property for an injection grout. However, apart from some doses of sepiolite the variation in yield stress is reasonably low. These two additives have opposing effects on the plastic viscosity: montmorillonite causes significant growth and sepiolite causes slight decrease with growing replacement rate. This would affect the flow velocity of the grout after the beginning of flow, where the faster flow, and therefore the addition of sepiolite, would be more advantageous. The addition of wollastonite addition led to the least significant changes in flow behaviour of lime-based grouts, while attapugite in most cases showed higher yield stress and plastic viscosity than other additives.

3.2 Amplitude sweep test

During the amplitude sweeps, the most notable changes in the variables were the increased value of the storage modulus in the viscoelastic region, representing a more pronounced viscoelastic solid behaviour due to the replacement of lime by mostly larger, needle-like particles. Secondly, the flow strain, value (the point where the transition from viscoelastic solid to liquid behaviour occurs, value) mostly increased, which in combination with a slightly lower, but for all the grouts similar, critical strain led to slightly more

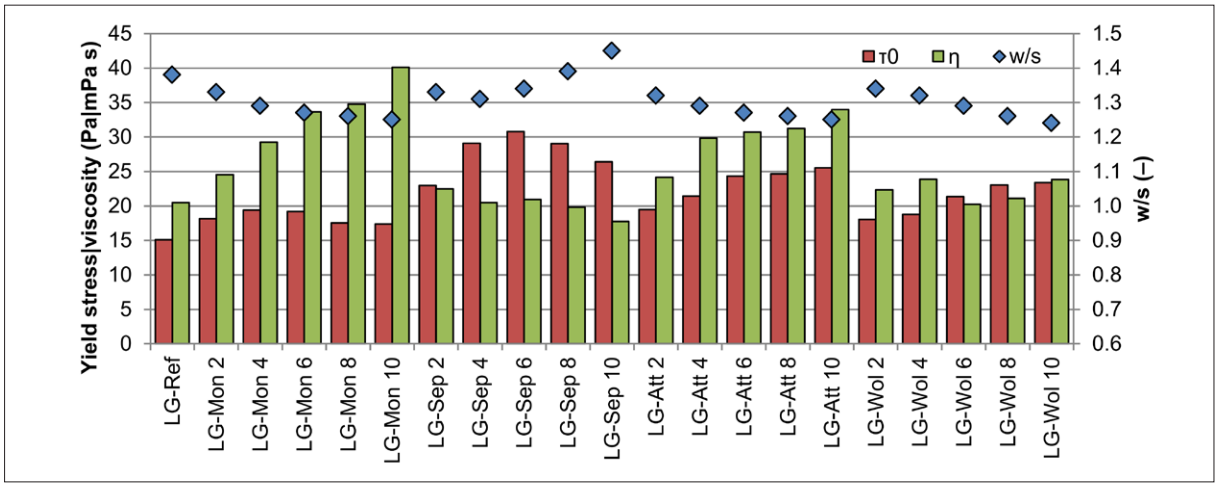

Table 1. Properties of dry raw materials.

homogenous and gradual breakdown of internal structure mainly for samples modified by sepiolite and attapugite.

4. Conclusions

All the natural rheology modifiers studied showed promising results for further utilization in lime-based injection grouts. InSepiolite, in particular sepiolite, may be suitable solely for its rheology modifying properties, while other additives seem to be more suitable as a combination of filler with added rheology modifying function and wollastonite, due the fibrous structure, also for improving the cohesion of the hardened grout. However, the impact of expansive clays (montmorillonite, sepiolite) on grout volume stability requires further investigation. The rheology modifying function of thesethe additives has to be taken into account while using them in the injection grouts regardless of their main purpose in the mixture.

Acknowledgement

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Exploring the Production of an Alternative Natural Hydraulic Lime Using Brazilian Dolomitic Filler and Kaolinitic Clay

1. Introduction

Natural hydraulic lime (NHL) is usually indicated for restoration and conservation of historical buildings and has been seen as a potential eco-friendly binder material compared to Portland cement, because of its lower calcination temperature (up to 1250°C) and CO2 reabsorption during hardening and setting. However, marly limestone, its raw material, is not available in all places and no studies were found investigating the effectiveness of combining dolomite and clay to produce a material analogous to NHL. Based on this, the calcination and slaking process of mixtures of Brazilian dolomitic filler and kaolinitic clay were explored by varying mixture shape, residence time and clay size fraction in calcination. XRD, TGA and FTIR were conducted to explore the products formation.

2. Materials

The materials used were dolomitic filler donated by Mibra Company located in Paraíba, Brazil and two different kaolinitic clay fractions, K200 (below 75µm) and K325 (below 45µm) donated by company Caulisa S.A located in Paraíba, Brazil. A commercial Natural Hydraulic Lime (NHL5) was also purchased to be used as a reference material. X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier Transform Infrared Spectrometry (FTIR) and laser granulometry were used to characterize these materials.

Dolomitic filler presented biggest grains with D50 and D90 of 23.9 µm and 58.7µm, while K200, K325 and NHL5 D50 values of 4.8 µm, 10.7 µm and 4.8 µm and D90 of 51.3. µm, 66.9 µm and 21.8 µm, respectively. Regarding to chemical composition, K200 and K325 kaolinitic clays XRF showed high percentages of silica (47.8-49.6%) and alumina (34.9-37.3%) and low iron content (0.2-0.3%), with a percentage of 80% of kaolinite content and an ordered structure according TGA and FTIR. XRD presented the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) and muscovite ($K_0.89Na_0.10Rb_0.01(Al_2.88Fe_0.02Mn_0.02)(Si_3.08Al_0.92)O_{10}(OH)_2$) as mineral phases. The dolomitic filler is formed by 92% of dolomite based on TGA and dolomite ($CaMg(CO_3)_2$) mineral presence was confirmed on XRD and FTIR. Percentage of CaO (30.9%) and MgO (22.6%) was found in XRF dolomitic filler results. Commercial NHL5 XRF presented high CaO (60.8%) and 2.9%, 12.4%, 4.1% and 1.6% of MgO, SiO2, Al2O3 and Fe2O3. Gehlenite ($Ca_2Al(AlSi)O_7$), portlandite ($Ca(OH)_2$), larnite (Ca_2SiO_4), periclase (MgO) and peroviskite ($CaFeTi_2O_6$) were found as mineral phases. NHL5 FTIR spectra matched previous studies, suggesting the presence of C_2S or C_3S. Three weight slopes of 11%, 1.3% and 2.2% were observed between at 402°C, 557°C and 627°C, respectively. And they can be linked to dehydroxylation of Mg(OH)2, Ca(OH)2 and calcium carbonate (CaCO3), based on usual temperatures of dehydroxylation and decarbonation[1].

1 Elsen et al. 2012.

3. Methods

Dolomitic filler was used as source of carbonates and kaolinitic clays as source of silica and alumina. In order to analyze the best conditions for calcination, the composition of 20%/80% of dolomitic filler/clay at 1250°C and heating rate of 14°C/min was fixed, material was calcined in powder and in spherical pellets and residence times of 30 min and 60 min were used. To evaluate the influence of different particle size of kaolinitic clays during calcination and solid reaction, all mixtures were tested with two kaolinitic clay fractions: K200 and K325, and presented in Groups K200 and K325, respectively. In total, there was 8 calcined mixtures and 8 calcined and slaked mixtures, where 4 of each set belongs to Group K200 and others to group K325.

Before calcination, powder was mixed for 2 min manually with a spoon and more 2 min of shaking inside a bag. For powder mixtures, 30g was added to alumina crucible and knocked to minimize distance between particles. For pellets, 25-30% of water was added to each powder composition, molded and weighed to produce spheres of 3g. These pellets were put in stove at 105°C ± 5°C for 24h to dry. Around 40g of dry pellets were inserted in furnace in alumina crucibles. After the residence time, mixtures were removed from furnace and were left to cool down in air for 3 hours.

After calcination, mixtures were crushed and sieved until particles below 75µm were obtained. For slaking process, 26% of water in relation to material weight was added to mixture and mixed for 5 min. This process involves heat release and at the end of process the mixture was still powder. Finally, mixtures were analyzed by XRD, TGA/DTG and FTIR before and after slaking process.

4. Results

TGA results showed that all samples were completely decarbonated considering that there were no weight losses after 750°C, temperature of dolomitic filler decarbonation. However, weight losses around 380°C and 500°C were observed in samples before slaking process, which can be related to the presence of calcium hydroxide Ca(OH)2 and magnesium hydroxide (Mg(OH)2). This can be justified by samples' exposure to air humidity during cooling. Samples after slaking process, presented a weight loss related to structural water loss of hydrated salts (possibly calcium silicate hydrate - CSH) at around 200-300°C besides the hydroxide's dehydroxylation losses and hygroscopic water loss1. Analyzing the effect of slaking process, samples of Group K200 calcined in powder and 30 min of residence time showed a higher susceptibility to transform oxides into hydroxides, with a final amount of around 17% of Mg(OH)2 and 17% of Ca(OH)2.

FTIR allowed to observe the possible presence of C2S (larnite), usual hydraulic compound of NHL. Bands in 849, 903, 997 cm-1 were seen in all samples and in reference material NHL5, and are related to silicate presence, as observed in previous studies[2]. Samples of Groups K200 and K325 had similar peaks, with sharper peaks for samples calcined in pellets. Comparing the residence time, 60 min seemed to be favorable to produce hydraulic compounds (shaper peaks), and this was more evident for Group K325.

Regarding to XRD results, Groups K200 and K325 had the same set of phases before slaking: Larnite (C2S), Gehlenite, Portlandite, Spinel, Periclase, Merwinite, Mayenite and Monticellite. After slaking, new phases were formed in addition to existent ones: Hydrotalcite, Brucite, Katoite, CSH and Hydrogarnet. No evident amorphous hump was seen in patterns. The XRD results confirmed the presence of larnite, brucite and portlandite as seen in FTIR and expected in TGA, respectively. However, no evidence of CaO and MgO was observed in calcined materials, probably because of air humidity what caused early hydration. Quantitative XRD was performed considering mixtures as completely crystalline. The presence of larnite was more evident for mixtures calcined in pellets with 60 min of residence time and using K200

2 Król et al. 2022.

clay, achieving the quantity of 36.9%. However, after slaking this percentage dropped to 21.3%. In relation to hydroxides compounds the maximum amount was observed for mixtures calcined in powder, 30 min of residence time and using clay K200, as in TGA results.

5. Conclusions

This study demonstrated the technical feasibility of producing a binder similar to natural hydraulic lime (NHL) from dolomitic filler and kaolinitic clay, where were obtained typical NHL hydraulic compounds such as C_2S and Gehlenite. The use of pellets—commonly formed in rotary kilns—proved effective in promoting the formation of calcium and magnesium hydroxides, as well as hydraulic phases. However, increasing the residence time and using finer clay fractions (K325) favored the formation of hydraulic phases while reducing the amount of hydroxides. Additionally, the slaking process significantly decreased the content of hydraulic and hydroxides compounds, what decreases the potential binder reactivity. These findings underscore the relevance of raw material selection and processing parameters in mineralogical composition and reactivity of alternative binder.

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RAVI CHANDRA MALLADI, THIRUMALINI SELVARAJ, MICHELE SECCO

Performance enhancement of various lime mortars through organic addition for heritage conservation: A comprehensive multi-analytical investigation

1. Introduction Paragraph

Lime-based cementitious systems have been extensively employed as binding materials in heritage structures for more than 10,000 years, remaining valuable construction components due to their favorable hygrothermal properties, specifically breathability and deformability characteristics[1]. Despite these advantages, lime binders exhibit several inherent limitations, including inferior mechanical resistance, delayed setting kinetics, compromised workability, and protracted carbonation processes. To address these deficiencies, ancient construction methodologies incorporated various organic additives to enhance performance parameters. The presence of organic derivatives specifically carbohydrates, polysaccharides, and proteinaceous compounds has been demonstrated to improve rheological properties, mechanical strength, carbonation kinetics, and durability characteristics of lime-based systems[2]. This investigation systematically evaluates the performance enhancement of diverse lime mortar formulations incorporating fermented organic additives predominantly utilized in the Indian subcontinent, employing multiple complementary analytical techniques to characterize the resulting modifications in material properties[3].

2. Materials and methods

This investigation utilized three distinct calcareous binders (air lime, dolomitic lime, and shell lime) in conjunction with two organic additives: kadukkai (Terminalia chebula) and jaggery (non-centrifugal cane sugar). The organic solution was prepared at a concentration of 2.5% weight per volume of each organic constituent to water and subjected to fermentation under semi-anaerobic conditions for a 7-day period. Six mortar formulations (detailed in Table 1) were synthesized according to IS 6932 Part 7 specifications, maintaining a 1:3 binder-to-aggregate ratio by mass, employing natural fluvial sand with a maximum particle size of 2.36 mm as the aggregate phase. All specimens underwent carbonation in ambient atmospheric conditions for a 365-day curing period. The mechanical properties of the specimens were evaluated through uniaxial compression testing, while mineralogical composition and microstructural characteristics were assessed utilizing multiple analytical methodologies, including X-ray diffraction (XRD), thermogravimetric analysis (TGA), and computed micro-tomography.

3. Results and discussion

Organic-modified mortars across all three lime variants demonstrated enhanced performance across all measured parameters. Air lime mortar exhibited a 24% increase in compressive strength accompanied by reductions of 3.8% and 33% in water absorption and porosity, respectively. Similarly, dolomitic and shell lime mortars incorporating organic additives showed significant improvements of 40% and 32%

1 Ravi et al. 2018.
2 Athira et al. 2024.
3 Maravelaki PN et al. 2023.

in compressive strength, with corresponding decreases of 4.6% and 20.7% in water absorption, and 44% and 21% in porosity. The polysaccharides and proteins present in the organic additives facilitated prolonged moisture retention within the mortar matrix, enhancing hydration product formation relative to reference specimens, while simultaneously inhibiting carbonate formation[4]. The elevated pore water content impeded carbon dioxide diffusion throughout the mortar matrix, resulting in decelerated carbonation kinetics compared to reference mortars, which facilitated controlled and uniform crystallization with diverse calcium carbonate polymorphs, including aragonite and vaterite, alongside stable calcite formation[5]. This sustained carbonation process generated homogeneous crystal distribution in conjunction with amorphous calcium carbonate (ACC), effectively occupying interstitial voids and consequently reducing overall porosity. Both pore volume and pore diameter were diminished in organic-modified mortar specimens relative to reference samples. The decreased standard deviation in structure separation measurements for organic-modified specimens confirms a more uniform pore distribution throughout the matrix.

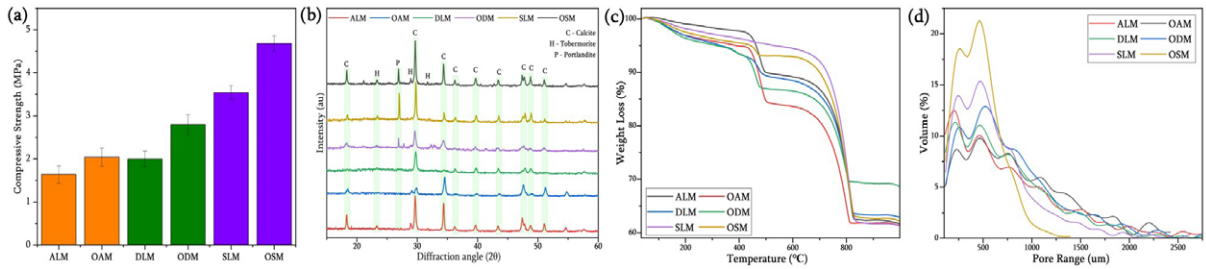

Figure 1. (a) Compressive Strength; (b) XRD analysis; (c) TGA analysis; (d) Porosity analysis

Specimen	Code	Water abs. (%)	Tomography		TGA quantification (%)		
			Total porosity	SD (St. Sp) - um	CaCO3	Hyd	Ca(OH)2
Air Lime Mortar	ALM	15,7	2,67	561,34	70,32	5,7	21,29
Organic Air Lime Mortar	OAM	15,1	1,77	532,88	60,46	10,51	29,03
Dolomitic Lime Mortar	DLM	14,9	4,56	485,86	72,42	15,15	12,42
Organic Dolomitic Lime Mortar	ODM	14,2	2,55	498,23	60,32	17,66	22,02
Shell Lime Mortar	SLM	8,2	3,18	410,33	88,03	8,24	3,73
Organic Shell Lime Mortar	OSM	6,5	2,49	224,88	83,48	10,11	6,42
* WA – Water absorption; SD(st.sp) - Standard deviation of structure separation; Hyd – Hydration products							

Table 1. Specimen description, water absorption, porosity and TGA phase quantification

4. Conclusions

The incorporation of kadukkai and jaggery-infused fermented organic water into conventional lime mortars of varying compositions significantly enhanced their mechanical properties, particularly compressive strength, through the augmented formation of hydration products that functioned as supplementary load-bearing phases alongside calcite. The gradual and sustained carbonation process observed in these organic-modified mortars facilitated the formation of amorphous calcium carbonate (ACC) and calcite with homogeneous crystallization patterns, resulting in optimal pore matrix filling and the development of a uniform microstructure. This refined microstructural arrangement effectively reduced critical parameters such as water absorption coefficient and porosity, thereby enhancing the durability characteristics

4 Malladi and Selvaraj 2023.
5 Malladi and Selvaraj 2024.

of the mortar compared to conventional lime-based systems. These improved performance attributes render the formulation particularly suitable for application in repair mortars for heritage conservation.

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Parametric design of self-healing admixtures for repair mortars of 20th century historic buildings

1. Introduction and rationale

Historic buildings of 20th century are the trademark of numerous European cities, towns and villages, forming a living symbol of Europe's rich historical and cultural background. As a living part of modern Europe, they are reflecting and shaping the identity of our local, national and multinational societies, making up 30% of the European building stock[1]. At the same time, 20th built heritage introduces a variety and combination of architectural, engineering and material innovations, associated with industrial revolution and the introduction of cement and steel in the construction sector. However, depending on the local tradition, cultural influences and technological exchanges, there is a vast variety of mortar mixtures that follow the evolution of building technology, such as lime-based mortars, NHL mortars, cement-based mortars, mixtures of lime with cement etc. This creates an inevitable need for tailoring the properties of conservation mortars, according to the architectural, conservation and durability requirements of different buildings, while simultaneously preserving aesthetic characteristics and architectural integrity[2].

Considering the paramount stock of historic buildings in the EU, the need to expand the service life of repair mortars and thus of historic buildings with minimum number of repairs during their lifespan is inevitable. To this end, the development of innovative self-healing admixtures that can multiply the limited potential of autogenic repair of conservation mortars offers a significant advantage towards the sustainable retrofitting of 20th century buildings. The development of autonomous self-healing repair mortars and concrete has also emerged as a favorable solution to extend the service life of historic concrete structures with minimal intervention.

This work focuses on development of core–shell inorganic admixtures for all types of repair mortars, which autonomously seal cracks when damage occur. What distinguishes this system is the ability for parametric design of admixtures, including capsule size, shell properties, core composition and affinity with different mortar matrices, able to meet both technical and aesthetic demands of repair mortars for preserving 20th century architectural heritage.

2. Research outcome

The self-healing admixtures are fabricated via the pan-coating technique. In this process, a mixture of hydraulic components forms small granules (1–4 mm) that serve as the reactive core of the admixtures. This core is coated with a cementitious slurry to form a protective outer shell, yielding spheroidal capsules up to ~6 mm in diameter. The shell composition can be modified by incorporating setting accelerators for enhancing shell density and strength. The self-healing admixtures are incorporate into repair mortars as partial aggregate replacement. Specifically, 5–20% of the sand volume can be substituted with capsules,

1 EU-Energy performance of buildings. https://ec.europa.eu/energy/en/topics/energyefficiency/buildings.
2 Torraca 2009.

without affecting the consistency/workability of the mixture or creating the need for changing the mix proportions[3].
In a study, we present the mechanical and microstructural characteristics of three types of repair mortars, namely cement-based, NHL-based and ternary mixtures (lime-cement-pozzolan) that incorporate a trial series of core-shell self-healing admixtures[3]. Quantitative assessments of their performance characteristics included capsule survivability after mixing and mechanical performance testing. Mortar prisms and cylinders were prepared with varying capsule contents to evaluate compressive and flexural strength, as well as healing efficiency[4] through crack closure observations and reductions in water uptake over a defined healing period. Experimental results showed that the inclusion of capsules did not alter their mechanical strength, while the addition of self-healing admixtures can reduce water absorption up to 75% after a 28-day healing period—compared to ~30% in capsule-free mixes. Finally, microscopic analyses confirmed crack filling and identified healing products such as calcium hydroxide, ettringite, and secondary C–S–H, supporting the system's effectiveness in self-sealing under exposure[5].

3. Discussion

The self-healing admixtures developed responds to the challenge of tailor-made healing agents that can be directly incorporated into the mass of different types of conservation/repair mortars. Specifically:
- Capsule size can be adjusted to match the aggregate distribution of the substrate, allowing the capsules to function as "invisible aggregates" that do not disrupt surface texture or workability.
- Shell composition can be tuned using additives such as sodium silicate to balance durability during mixing with brittleness under stress, ensuring that the capsules remain intact during placement but rupture efficiently when intersected by a crack.
- Trigger sensitivity can be designed to ensure that cracks do not propagate around the capsule but instead activate the healing mechanism through direct intersection and rupture.
- Core chemistry can be modified to suit the binder system of the host mortar—e.g., OPC, lime, pozzolanic, or blended compositions—ensuring chemical compatibility and promoting the integration of healing products such as calcium-silicate-hydrate (C–S–H), ettringite, and eventually calcite.
- Core functionality can also be differentiated by introducing other performance-enhancing agents beyond self-healing.

By adjusting these parameters, conservation scientists and engineers can adapt the repair mortar system to the needs of each type of building—whether that means targeting permeability reduction in exposed façades, enhancing strength recovery in load-bearing elements, or achieving visual neutrality in surface treatments. The proposed technology can not only extend the service life of interventions, reducing the need for future repairs, but also significantly lower the embedded CO_2 associated with repeated repair cycles. In historic contexts, this translates into fewer maintenance interventions and less visual disruption over time, ensuring that the original design and material expression are preserved with minimal alteration. Additionally, by limiting material consumption across a building's lifecycle, the system contributes to reduced environmental impact and aligns with sustainability goals in architectural conservation.

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3 Papaioannou et al. 2022.
4 Papaioannou et al. 2023.
5 Karatasios et al. 2024.

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Effect of metakaolin dosage on the rheological behaviour oh hydrated lime-based mixtures

1. Introduction

Lime-based mortars are commonly employed in the restoration and conservation of historic buildings due to their compatibility with the traditional materials originally used in such constructions. The incorporation of pozzolanic additions contributes to the enhancement of properties such as permeability, durability, and mechanical strength, thereby increasing the overall performance and suitability of the mixtures for application in heritage interventions. In this context, the objective of this study is to evaluate the influence of incorporating different metakaolin contents on the rheological properties of hydrated lime-based pastes and mortars.

2. Experimental Program

The first stage of the methodology consists of the physical, chemical, mineralogical, and microstructural characterization of the materials, followed by the formulation of paste and mortar mixtures, which will be evaluated in terms of their rheological properties.

2.1 Materials

Pastes composed of hydrated lime and metakaolin (MK) were prepared with replacement levels of 40%, 50%, and 60% of lime by the specified pozzolan, adopting a fixed water/binder ratio of 1.0, in accordance with the literature[1,2]. For the mortars, the same metakaolin contents were employed, and a binder:aggregate ratio of 1:3 by mass was established.

The physical characterization of the materials was conducted through tests for specific gravity, bulk density, and laser diffraction particle size distribution. The chemical composition was analyzed by X-ray Fluorescence (XRF), while the mineralogical and microstructural characteristics were assessed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively.

2.2 Methodos

The pastes were subjected to the mini slump test using a mini cone shaped as a reduced Abrams cone, with dimensions of 19 mm for the top diameter, 38 mm for the bottom diameter, and a height of 64 mm. Additionally, rotational rheometry tests were carried out using the HAAKE MARS (Modular Advanced Rheometer System), equipped with a parallel plate geometry of 35 mm diameter, and operated under controlled temperature conditions of 25°C.

The arheological testing procedure followed methodologies found in the literatura[3]. Prior to each test, a pre-shear stress of 50 Pa was applied for 45 seconds in order to eliminate residual stresses and deformations. Following this step, the paste was allowed to rest for 60 seconds before the test commenced. To

1 Sales et al. 2021.
2 Zhang et al. 2020.
3 Arizzi, Banfill 2019.

determine the viscosity and shear stress, the test was conducted under a variable shear rate ranging from 1.5 to 510 s^{-1} over a period of 330 seconds. The shear rate increased in the following sequence: 1.5; 3.1; 5.1; 10.2; 51.1; 102; 153; 170; 306; 340; 510 s^{-1}, with each step maintained for 30 seconds to ensure stabilization. The deceleration phase followed the same pattern, decreasing the shear rate from 510 to 1.5 s^{-1} with identical time intervals.
For the mortars, the water content of each mixture was determined by targeting a fixed flow value of 260 ± 5 mm, measured using the standard flow table test. Once this consistency was achieved, the mixtures were evaluated through the squeeze-flow test, conducted with a Shimadzu universal testing machine equipped with a 10 kN load cell. The tests were performed at two displacement rates: 3 mm/s at 10 and 60 minutes, and 0.1 mm/s at 15 and 65 minutes, following the procedures established by the relevant standard.

3. Results and Discussion

For the pastes, a reduction in flow was observed in the mini slump test as the metakaolin content increased. Figure 1a presents the results of the descending curve of Shear Stress versus Shear Rate, while Figure 1b presents the results obtained by the squeeze flow test for 15 and 65 min at a speed of 0.1 mm. The results obtained from the rheometer tests indicate that all paste samples exhibit non-Newtonian fluid behavior, characterized by an initial yield stress, decreasing viscosity with increasing shear rate, and non-linear flow curves. Additionally, the presence of thixotropic behavior is evidenced by the hysteresis loop areas[4]. It was observed that as the metakaolin content increases, the shear stress values also rise, maintaining a directly proportional relationship across the samples. These findings are consistent with the mini slump test results.
For the mortars, the water/binder ratio obtained was 1.0 for all mixtures, considering the previously fixed spread. Regarding the squeeze-flow analyses, the results indicate a slight progressive stiffening of the mixtures over time (from 15 to 65 minutes), as well as an increase in rigidity with the rise in pozzolan content, as presented in Figure 1b.

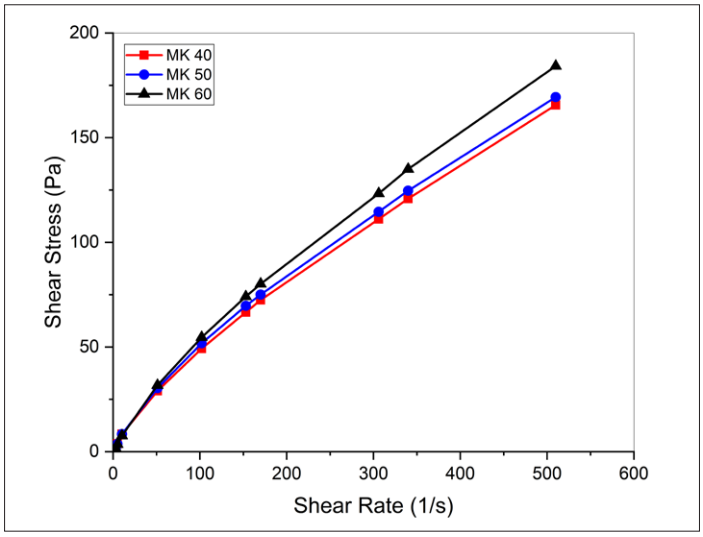

Figure 1. (a) Shear Stress versus Shear Rate of the pastes. (b) Squeeze flow of the mortars at 15 and 65 minutes.

4. Conclusions

Based on the results, it is observed that the metakaolin content significantly impacts the rheology of hydrated lime-based mixtures, leading to increased viscosity and shear stress at a given shear rate, in addition to promoting greater stiffening of the mixtures over time.

4 Sato 2015.

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Predictive multiscale design of mortars with improved thermal performance

1. Introduction

The development of sustainable retrofitting materials for heritage buildings demands innovative design approaches that balance improved thermal performance, material compatibility, and environmental impact. ThisPredictive material design to tackle these key heritage conservation challenges can be achieved via coupling multiscale numerical modelling and state-of-the art data driven approaches. While numerical homogenization methods have been presented in the literature to perform single upscaling (e.g. from properties of the constituents to properties of the resulting mortar), no framework has been presented that simultaneously considers different scales. To fill this gap, this work presents a predictive multiscale modelling framework for optimizing cementitious mortars enhanced with phase change materials (PCMs), aiming to support low-carbon retrofitting strategies.providing a tool that predicts the performance of a retrofitted wall based on the mix design at the microscale – hence bridging the gap between material and structural scale design. The proposed methodology integrates high-fidelity finite element models, analytical homogenization techniques, and data-driven tools to assess and optimize the thermal, mechanical, and environmental performance of mortars at multiple length scales.

2. Methods

The modelling framework is structured around three sequential upscaling steps: from microstructure to mortar, from mortar to wall element, and from wall element to the building envelope. At the microscale, representative volume elements (RVEs) simulate the random spatial distribution of PCM inclusions within the cement matrix (Figure 1). These models, based on the heat capacity method for simulating phase change, calculate the effective thermal conductivity for a range of inclusion geometries and volume fractions. The mesoscale models build upon the homogenized cement-PCM matrix by incorporating natural sand aggregates, enabling the assessment of additional heterogeneity. The results have been validated via comparison with analytical solutions in cases where such models are known to provide accurate predictions (see Figure 2). Parametric studies explore the effects of sand volume fraction, distribution, and intrinsic thermal properties, considering realistic ranges of material parameters derived from existing literature (Table 1). Table 1 also reports a sample mix design developed within the present project. At

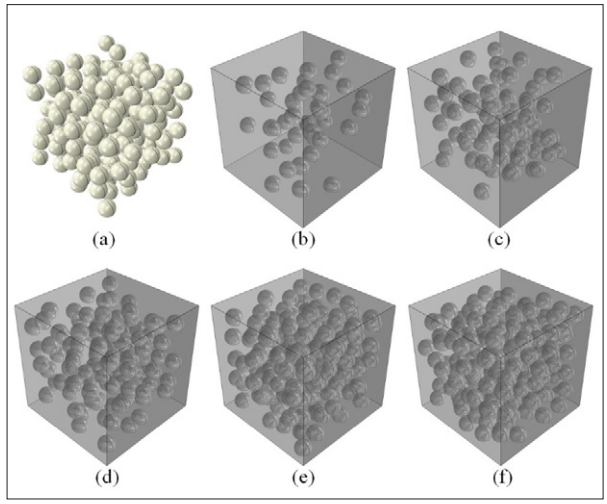

Figure 1 3D representation of different parts: (a) PCM capsules for vol. fraction of 25%, and composite samples for volume fractions of (b) 5%, (c) 11.25%, (d) 17.5%, (e) 23.75%, and (f) 30%.

the macroscale, a 1D finite element model simulates heat transfer in layered wall assemblies using outputs from previous scales.
To enable broad usability, the high-fidelity simulation results are employed to train artificial neural networks, forming the basis of a fast-running predictive tool embedded in a user-friendly web application.

3. Results and conclusions

Validation of the proposed framework against analytical solutions and literature data demonstrates strong agreement and confirms the accuracy of the proposed multiscale approach (see, e.g., Figure 2). The developed multiscale framework offers a robust, predictive capability for designing PCM-enhanced mortars tailored for heritage retrofitting. Particularly, it enables material decisions thatto enhance energy efficiency, reduce operational and embodied carbon, and support circular economy principles through integration of recycled constituents.reduce costs. Future developments will integrate experimental data from ongoing work within the SINCERE project to further calibrate and validate the models. By bridging material-scale simulations with building-scale performance assessment, the framework provides a practical and scientifically grounded tool for sustainable retrofitting of historic structures, fostering informed decision-making across engineering, conservation, and policy domains.

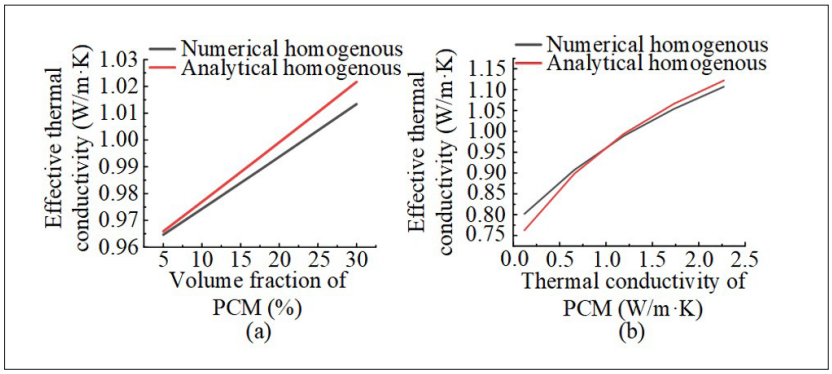

Figure 2. Numerical vs. analytical (Maxwell, 1873) homogenization at the microscale

Range of parameters in numerical models			
Constituent	Parameter	Unit	Range considered
PCM	Diameter	mm	0.001 – 1 (Khattari et al. 2020)
PCM	Thermal conductivity	W/(m·K)	0.12 – 2.27 (Han et al. 2022; Rolka et al. 2024)
PCM	Volume fraction (per unit volume of paste)	%	5 – 48 (Liu et al. 2020; Wang et al. 2022)
Cement paste	Thermal conductivity	W/(m·K)	0.53 – 1.38 (Ricklefs et al. 2017)
Sand	Thermal conductivity	W/(m·K)	0.48 – 0.56 (Chen 2008)
Sand	Volume fraction (per unit volume of mortar)	%	20 – 68 (Yousefi et al. 2021)
Sample mix design developed within the project			
Constituent	Parameter	Unit	Value
Cement CEM IV	Mass content per unit volume	Kg/m³	882
Pozzolana	Mass content per unit volume	Kg/m³	90
Water	Mass content per unit volume	Kg/m³	192
SP XA2305_10	Mass content per unit volume	Kg/m³	41
Sand	Mass content per unit volume	Kg/m³	1172
Fiber	Mass content per unit volume	Kg/m³	86
PCM	Mass content per unit volume	Kg/m³	22
Crystalline admixture	Mass content per unit volume	Kg/m³	7

Table 1. Range of parameters considered in numerical models and sample mix design developed within the project

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Green-labelled ready-mixed plasters for the preservation of the architectural heritage: a critical evaluation

1. Introduction

Ready mixed plasters are widely used in heritage restoration and many Italian companies market this kind of product as "green". While some provide environmental product declarations (EPDs) to support their green claims, others rely on vague certifications, raising concerns of greenwashing. Green-labelled ready-mixed plasters (GLRMP) for conservation purposes are lime (HL) or natural hydraulic lime (NHL) based and should be cement-free. However, an analysis of Italian manufacturers' catalogues reveals that many of them contain cement, generally not clearly declared. This lack of transparency complicates sustainability assessments and raises doubts about compatibility with historic masonry. Applying the definitions of "green product" found in literature[1] to the plasters for architectural heritage preservation, emerge that mixtures should minimise environmental impact throughout its life cycle, use low-impact or recycled materials, prioritise local resources and ensure durability and compatibility. The study assesess the physical and mechanical properties, resistance to freeze-thaw (FT) cycles and salt crystallisation (SC) and environmental impact through life cycle assessment (LCA) of five GLRMP, to propose a critical discussion on their potential environmental benefits or if serve as a marketing tool, questioning their real sustainability in architectural heritage restoration.

2. Materials and methods

Five NHL-based plasters labelled as green and formulated for restoration were analysed (composition in Table 1). For SC tests, 1 cm of plaster layers were applied to 30×30 cm brick masonry samples.
The characterisation analysis performed were the flexural and compressive tests[2], the capillary rise tests[3] and the porosity evaluation with a mercury intrusion porosimeter (MIP); the durability test carried out were FT cycles[4] and SC[5]. LCA evaluated the plaster's environmental impact (cradle-to-gate) for 1m2 coverage (1cm thick). Due to company confidentiality, the primary data were only the mixture composition and transport distances -except for I2-. Those, combined with secondary data (from the SDS and Ecoinvent 3.10) were analyzed using SimaPro 9.6.0.1 and applying EN 15804 +A2 (adapted) 1.01 / EF 3.1 impact assessment method.

3. Results

The analysis of plasters confirms that the type of binder significantly influences their physical and mechanical properties: CSA based plaster showed higher mechanical strength, lower porosity and less cap-

1 Sdrolia, Zarotiadis 2019.
2 EN 1015-11, 2019.
3 EN 1015-18, 2004.
4 EN 11186, 2008.
5 RILEM MS-A1, 1998.

Information and characteristic	I1	I2	I3	I4	I5
Binder used	CSA; HL, NHL 5	NHL 3.5	NHL 5	NHL 5	NHL 5
Aggregate used	S, C	S, C, P	C, D	S, C	C
Water in 25 kg [L]	4	5.1	5.5	4.75	5
Flexural (F) // compressive (C) strength [N/mm^2]	(F) 3.33 ± 0.56 (C) 16.3 ± 0.68	(F) 1.12 ± 0.26 (C) 3.00 ± 0.94	(F) 0.82 ±0.04 (C) 1.46 ± 0.06	(F) 0.43 ±0.06 (C) 1.35 ± 0.09	(F) 0.88 ±0.01 (C) 1.33 ± 0.07
CRC [(kg/m^2 min$^{0.5}$)^{24h}]	1.44 ± 0.10	2.30 ± 0.13	22.58 ± 0.50	22.40 ± 0.41	20.84 ± 0.44
Total open porosity [%] (P) average pore diameter [µm] (ø)	(P) 23.50 (ø) 0.08	(P) 45.90 (ø) 19,40	(P) 43.52 (ø) 1.72	(P) 31.36 (ø) 1.22	(P) 31.01 (ø) 1.59
FT test	PASSED	PASSED	FAILED	FAILED	FAILED
SC test	FAILED	FAILED	PASSED	PASSED	PASSED

Table 1. Plasters composition and average results obtained by the physical, mechanical and durability tests. Legenda; CSA= clinker sulfoalluminate; S= silica sand; C= calcareous sand; P= pozzolana; D= dolomitic sand; CRC= capillary rise coefficient. Durability tests are classified as FAILED in the case of severe degradation and PASSED for slight deterioration pattern.

illary rise, while NHL plasters showed the opposite behaviour. The pore structure also plays a key role in durability: plasters with very fine (I1) or large (I2) pores showed lower CRC, limiting fluid transport within the material. This property proved advantageous for resistance to temperature variations (Figure 1A), as I1 and I2 suffered minimal damage after freeze-thaw (FT) cycles, remaining largely intact. In contrast, I3 and I4 were completely destroyed. The fluid transport properties, however, have different implications for salt crystallisation: plasters with high CRC (I3, I4 and I5) facilitated the outward migration of salt solutions, leading to the formation of efflorescence. Conversely, I1 and I2 restricted fluid movement due to capillary pressure, leading to the formation of sub-florescence at the masonry-plaster interface, causing cracking, deformation and detachments (Figure 1B).
The environmental assessment provided insights into the sustainability of these materials. Due to the limitations of the data provided by the manufacturers, a precise quantification was not possible but general trends emerged: in the non-transport scenario (Figure 1C), I3 had the highest environmental impact for all the indicators. Additionally, it emerges that the plaster production weight mainly on the climate change, freshwater eutrophication and use of fossil resources indicators. In contrast, in the transport scenario (Figure 1D), I5 showed the highest overall environmental impact due to the procurement of raw materials over long distances. In contrast, I3, which relied on locally sourced materials (<8 km), showed the lowest

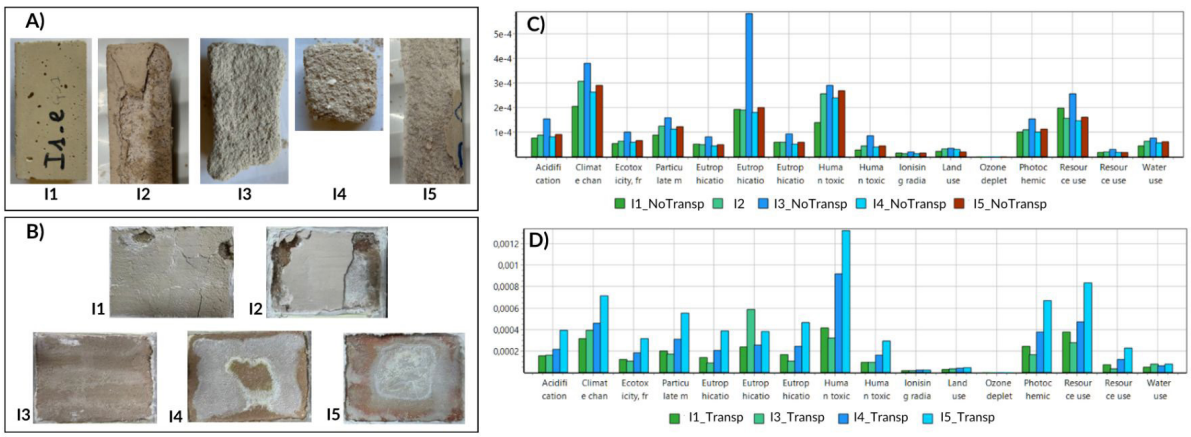

Figure 1. Aspect of the plasters at the end of the durability test and environmental profile related to the production process of the mixtures. A) Specimens subjected to FT cycles; B) Plasters applied on masonry mock-ups and subjected to SC test; Environmental impact related to the mixtures production without transport contribute-no transport scenario (C) and with transport contribution-transport scenario (D).

overall environmental impact. Transport had the greatest influence on human carcinogenic toxicity, fossil resource use, photochemical ozone creation and climate change.

4. Conclusions

The study underlines the complexity of assessing the sustainability of plasters for heritage conservation. Although some mixtures appear to be greener than others -based only on material composition-, a broader assessment that include materials' transport emissions or energy sources used in production, reveals a more nuanced picture.

In conservation practice, the historical context must be prioritised: original materials, construction methods and site-specific environment influence the success of a restoration project and the use of an incompatible or low durability plaster may lead to further damage, requiring additional repairs and increasing the footprint of the intervention.

Although the development of greener plaster is crucial, restoration must be evaluated holistically: in some cases, a formulation with a higher initial environmental footprint may be necessary if it ensures compatibility with historic substrates, meets local conditions and guarantees durability. Conversely, a plaster that appears environmentally friendly but has inadequate longevity or compatibility may result in a higher environmental cost.

A truly sustainable approach must balance material sustainability, historical compatibility and durability, ensuring that restoration efforts support both heritage conservation and environmental responsibility.

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Innovative mortar applications for the retrofitting of modern heritage buildings

1. Abstract

The conservation and adaptive reuse of heritage buildings present critical challenges in balancing historical preservation with modern energy and structural requirements. This research presents a comparative study of five pilot interventions from the EU-funded SINCERE project, each employing innovative mortar technologies tailored to the climatic, structural, and regulatory contexts of heritage structures in Israel, Spain, Czech Republic, Greece, and Malta. The case studies include mock-ups at Demo Park in Madrid as a testbed, a brutalist-style university building in Holon, an industrial steel-framed building in Ostrava, a neoclassical Ottoman school in Rhodes, and an early 20th century coastal searchlight post in Malta.

Across the sites, mortars incorporating hempcrete, textile reinforcement, and phase-change materials among other constituents are evaluated for their performance in thermal retrofitting, environmental resilience, and heritage compatibility. For the data on thermal performance, the network of sensors is applied. The Madrid pilot offers a controlled experimental setup through four full-scale mock-ups, allowing side-by-side performance comparison of different mortar formulations under real climatic conditions. In the Rhodes and Ostrava pilot pro, materials are integrated within conservation frameworks sensitive to national heritage regulations. Holon site tests the feasibility of retrofitting inhabited structures without altering their heritage value or disrupting daily use. The Malta pilot, situated in an aggressive marine environment, offers valuable insight into the performance of repair mortars on concrete surfaces, exposed to salt crystallization, and thermal renders on limestone masonry.

This research highlights how advanced mortars can enhance energy efficiency and material resilience while maintaining architectural authenticity. The results are intended to underscore the importance of specific material design, passive energy strategies, and scalable monitoring tools in achieving sustainable heritage retrofitting, contributing to a toolkit for conservation.

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State of the Art Report of the RILEM Technical Committee 277-LHS: Specifications for testing and evaluation of lime-based repair materials for historic structures

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Lime-based Repair Materials for Historic Structures: State of the Art Report of RILEM TC 277-LHS

Test procedures for repair mortars and grouts used in historic structures (HS) currently follow standards established for cement-based composites. This usually leads to erroneous results, as the aforementioned procedures are based on certain technical assumptions which are valid only for modern calcium-silicate cement-based binders. Furthermore, existing EN standards for lime (EN 459) and mortars (EN 1015), do not address specific issues related to lime-based mortars and grouts, such as mixing and stirring scenarios, slow setting and hardening, optimum time for testing mechanical characteristics and physical properties, durability (wetting-drying, freezing-thawing, sulphate attack etc.) testing. Therefore, laboratories dealing with the aforementioned materials often have to modify existing standard procedures referring to other materials to address their needs. This inevitably leads to experimental results from different laboratories and/or the industry, which are not easily or directly comparable.

RILEM TC 277-LHS was established back in 2017 with the primary aim of adapting/modifying existing test procedures for repair mortars and grouts to render them more realistic in terms of describing the properties, the behaviour and the performance of non-cementitious binders (e.g. lime, lime-pozzolana, NHL). This was achieved through a scientific network of experts, young researchers, practitioners and other stakeholders, with long-term experience in testing lime-based repair mortars/grouts. The aforementioned group of >40 people first made a critical review of existing knowledge and relevant standards. This led to two review/reports: one on the mechanisms of setting and hardening of lime-based binding systems[1] and one on additives and admixtures for modern lime-based mortars[2]. Much emphasis was placed on the durability of lime-based repair/repointing mortars, both in terms of testing, but also in terms of practical experience (i.e., positive and negative/damage cases)[3,4]. A sub-group of people participating in RILEM TC 277-LHS elaborated on the properties of lime-based renders and plasters, focusing on current test methods and suggesting ways for their improvement[5]. Last but not least, Pavia et al[6]. produced a report on hot-lime-mixed mortars; this paper was selected by Materials and Structures board of editors among the 10 best/outstanding papers published by the journal in 2023.

Currently, the members of RILEM TC 277-LHS are working on a State-of-the-Art Report on lime-based repair materials (mortars and grouts) for historic structures, that will place emphasis on testing their quality and performance. The report, which is scheduled to be published by the end of 2025,

1 Alvarez et al. 2021, 54(2):63.
2 Maravelaki et al. 2023, 56:106.
3 Papayianni, Hughes 2018, 135-139.
4 Groot et al. 2022, 55:10.
5 Veiga et al. 2023, 56:70.
6 Pavia et al. 2023, 56:87.

will comprise of seven (7) chapters. Chapter 1 will refer to the current principles of HS restoration and the use of lime-based materials in repairing HS (including reference to failures in restoring with cement-based materials, based on personal experience and the literature. This chapter will also include present day challenges, such as the impact of the quality of repair materials and concurrent implications on economy and sustainability. Chapter 2 will focus on the characteristics of commercial and custom-made lime-based mortars and grouts, whilst Chapter 3 will comprise a review of the basic regulative framework (i.e., Eurocode 6 – Part 2, EN 998-1, EN 13914-1 etc.) concerning masonry and materials, especially in relation to its applicability in the case of lime-based materials for the repair of HS. Chapter 4 will focus on the suitability of raw materials for the manufacture of lime-based mortars and grouts, whilst Chapter 5 will include currently used testing methods for characterizing the properties of lime-based mortars and grouts in the fresh state, together with critical comments and suggestions for their improvement. Similarly, in Chapter 6, currently used testing methods for characterizing the properties of lime-based mortars and grouts in the hardened state will be critically reviewed; this chapter will also include sub-sections on current and innovative test methods for testing the durability and thermal properties of lime-based repair mortars, as well as a sub-section on enhancing the adhesion of lime-based grouts to the substrate. Last but not least, Chapter 7 will provide much needed guidelines/instructions for the application of lime-based repair materials (mortars and grouts). These will include reference to storage/handling conditions, specific tools and equipment for the application of the aforementioned materials, any preparatory work deemed necessary, curing etc. Suggestions for field tests to be carried out before, during and after the execution of repair works will also be included in this last chapter, together with an indicative plan for the long-term monitoring of the behaviour/performance of repair interventions.

The aforementioned State-of-the-Art Report aims primarily at contributing and improving current testing methods regarding repair mortars/grouts. This is, in fact, a basic requirement for the building conservation practice, which is still pending. The State-of-the-Art Report will suggest (among other things) a set of modified laboratory and field procedures for testing the quality of mortars and grouts used in almost all repair interventions. This is anticipated to advance the level of repair works to the benefit of global economy and the longevity of HS.

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Adhesion: a paramount property for injection grouts. Review of standards and new testing methods

1. The importance of adhesion and its testing

Injection grouting is a critical intervention to stabilise delaminated plaster. It introduces in the stratigraphy a chemically and physico-mechanically compatible, adhesive material with bulking properties (the grout), re-establishing adhesion between plaster layers or between support and plaster layer[1-2]. Adhesion is therefore, by definition, a crucial property for grouts. Nonetheless, typically a thorough assessment of fresh properties is performed, as well as evaluation of hardened properties with comparison of different grout mixtures[3-4], but the assessment of adhesion is often overlooked. This paper aims to review adhesion testing of grouts and to discuss the different methodologies and procedures adopted, focusing on lime-based grouts.

2. Testing adhesion: a review

Physico-mechanical properties of grouts are typically tested with samples solely composed of the hardened grout, and they can be assessed with field or laboratory, qualitative or quantitative testing.
Adhesion is defined as the maximum tensile strength with direct load (pull-off) perpendicular to the surface of the tested material applied on the support[5]. Adhesion testing needs to involve therefore, by definition, not just the grout, but also (at least) the substrate to which it is applied.

2.1 Qualitative testing

Field testing typically uses a simplified set up/procedure compared to laboratory testing; even if it is just qualitative or semi-quantitative (and still, quantitative field tests exist), it can provide very informative data.
Mortar cups are used to assess the shrinkage of grouts (and therefore adhesion to its walls) in a porous support. The mortar cup can simulate the original plaster and can be pre-wet to simulate the pre-wetting on site[6]. To simulate a closed pocket (grout between two layers), the cup can be covered with a slab of plaster while drying and it can be excavated once hardened to assess shrinkage also in depth[6]. Grouted replicas of delaminated plaster can be produced and assessed qualitatively, cutting them and observing the adhesion in cross section[7-8].

1 Papayianni et al. 2023.
2 Biçer-Şimşir and Rainer 2013.
3 Padovnik et al. 2016.
4 Pachta and Goulas 2020.
5 N 1015-12: 2020.
6 Pasian, Martin de Fonjaudran, Rava 2020.
7 Pasian et al. 2017.
8 Potskhishvili et al. 2022.

2.2 Quantitative testing

Standard EN 1015-12 is designed to test adhesion of hardened mortars on substrates. It has been applied also for adhesion testing of grouts on a support. This is not representative of a real case, though, in which the grout hardens between two layers. Proposals have been made of multi-layers systems, in which the grout is injected between two plaster layers in heterogenous panels, and where adhesion is tested with EN 1015-123[9]. While such panels have multiple interfaces and their testing requires drilling, potentially having an influence on the result, new proposed systems are composed of 3 layers (plaster-grout-plaster) and describe a repeatable and reproducible sample preparation, with a pull-off testing without drilling[10-11]. Main differences in the procedure are listed in Table 1.

Standard/Ref. with procedure	System tested	Sample preparation	Load bearing	Standard applied/ modified
EN 1015-12	Support-grout	Core sample drilled	Ø 50 mm	EN 1015-12
Pasian et al. 2019	Plaster-grout-plaster	Grout injected between two plaster layers; Sample prepared in plastic container, then extracted; Grout layer exposed	Ø 95 mm	DIN 1048-2
Padovnik and Bokan-Bosiljkov 2022	Plaster-grout-plaster	Grout injected between two plaster layers; Grout injected in a pocket between plaster layers	Ø 100 mm	EN 1015-12
Standard/Ref. with procedure	**System tested**	**Sample preparation**	**Load bearing**	**Standard applied/ modified**
EN 1015-12	Support-grout	Core sample drilled	Ø 50 mm	EN 1015-12
Pasian et al. 2019	Plaster-grout-plaster	Grout injected between two plaster layers; Sample prepared in plastic container, then extracted; Grout layer exposed	Ø 95 mm	DIN 1048-2
Padovnik and Bokan-Bosiljkov 2022	Plaster-grout-plaster	Grout injected between two plaster layers; Grout injected in a pocket between plaster layers	Ø 100 mm	EN 1015-12

Table 1. Comparison of adhesion tests

Adhesion of the grout can be also assessed via a shear bond strength test: a test is proposed with the grout hardening between two stone layers.

3. Discussion and conclusions

The procedures proposed for the 3-layer sandwich samples, overall improve the accuracy of the test, since they do not require drilling -which may influence the grout adhesion and cohesion with vibrations- and they provide a bigger load bearing. Moreover, they are versatile, since the plaster can potentially reproduce the one(s) present on site. The sample preparation of one method ensures an easier check for sample homogeneity; while the sample preparation of the other method is more representative of a real case in terms of access of air for carbonation.

Adhesion is a crucial property for grouts, and its improved testing accuracy can provide important information for the chioce of materials to implement on site.

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9 Azeteiro et al. 2014.

10 Pasian et al. 2019.

11 Padovnik and Bokan-Bosiljkov 2022.

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Testing and requirements of the fresh and hardened state properties of lime-based grouts for the consolidation of architectural surfaces

1. Introduction

Architectural surfaces include a variety of decoration means and works of art, often found in heritage structures and applied in walls, floors and roofs. They usually refer to murals, mosaics (wall and floor), reliefs, as well as plasters and renders. They consist of the decorative surface and the substrate, firmly attached to the substructure (wall, roof, floor). The substrate is usually characterised by a multilayer structure, formed by 2-4 mortar layers, whilst its stratigraphy and typology depend on the decorative type (mural, wall or floor mosaic) and the wider technological aspects of each historic era and region. The thickness of the mortar layers was usually reduced to the outer surface, as well as the aggregates size and proportion. Mortar layers were mainly based on lime, including pozzolanic materials (natural and artificial), as well as other additives and admixtures (i.e. pieces of wood, reed, straw, natural resins). The aim was to enhance their overall performance, including volume stability, strength and resistance to humidity. Such aspects guaranteed the durability of the architectural surfaces, towards time, environmental conditions and loading (in the case of floors).

Nowadays they often confront several damages, concerning delamination and detachment of the mortar layers, both in their interface or in their conjunction with the substructure. This may be attributed to voids and discontinuities created in the mortar layers, due to multiple reasons (i.e. cracking, humidity, materials' deterioration). During conservation, a significant goal is to re-attach the mortar layers, stabilize their structure and fill the voids. To this direction, grouting is widely applied, concerning an irreversible, on-site repair technique, requiring specialized personnel (scientists and technicians), accurate application and highly effective injection materials.

Usually, custom-made and ready-mixed grouts are used, taking into account the issues of compatibility with the existing building materials. To this direction, lime-based grouts are applied, whilst their fresh and hardened state properties guarantee their performance, applicability and efficacy.

2. Fresh state properties of grouts

The fresh state properties of grouts define their efficient applicability, as well as their volumetric characteristics throughout setting. The water content, as well as the grain size of their constituents governs their performance, whilst various additives and admixtures may be inserted (i.e. superplasticizers, resins, ethanol, glass particles, fibers). The main properties tested at the fresh state include fluidity, injectability and volume stability either measured following relevant standards or tailored made on-site techniques.

Standards mainly refer to cement-based grouts applied in the concrete industry and as a result their appliance to lime-based mixtures requires modifications and further analysis testing. ASTM C939-02 and EN 445 concern fluidity, measured through the time (sec) for a specific grout quantity (EN 445: 1000ml ASTM C939-02: 1725ml) to pass a specific size cone under stated conditions. EN 1771 refers to injectability, thus the ability of a grout to penetrate into a capillary system and its adhesive capacity through splitting strength testing of the deriving specimens. Finally, ASTM C940-98a determines the expansion and accumulation of bleed water of grouts, during the first hours after their manufacture.

The upper and lower limits for testing the fluidity and injectability of the grouts generally depend on the characteristics of the substrate, as well as its preservation state (type and extent of pathology symptoms).
Regarding on-site testing, Simsir et al. developed a field method for classifying the fluidity and injectability of lime-based grouts for the consolidation of architectural surfaces, through the syringe test. For identifying the volumetric characteristics during the setting time of grouts Simsir et al. and Padovnik et al., developed a testing method for assessing their early shrinkage tendency.

3. Hardened state properties of grouts

The hardened state properties of grouts include a variety of parameters determining their overall performance. To this extent, the initial low strength level of lime-based grouts should be taken into consideration, as well as their slow strength development rate. Relevant experimental results show that the strength of lime-based grouts is steadily increased up to the age of 180 days, often rendering the typical 28d strength non representative. On the other hand, the grouts' mechanical properties should be respective to the strength rate of the substrate mortar layers, which is usually low. To this direction, high strength hydraulic grouts should be avoided, in order to fulfil compatibility requirements.
Regarding hardened state properties, relevant standards are usually followed, which however focus on lime-based mortars. EN1015-11 prescribes flexural strength (three-point loading of specimens up to failure) and compressive strength (testing of the two parts resulting from the flexural strength test) testing, using 4*4*16cm specimens. The curing conditions are important to be taken into account, due to the high water content of the mixtures leading to shrinkage phenomena and cracking. On the other hand, for testing physical properties, including porosity, water absorption, apparent specific gravity, water absorption coefficient, various regulative frames are followed, such as RILEM CPC 11.3, ASTM C1403-15, EN 1015-18 etc. According to literature, shrinkage deformations measured up to the age of 60 days, are usually tested through mass and volume change measurements.
The adhesive capacity of the grouts focusing on restoring historic architectural surfaces should be properly measured, both on the laboratory and on-site scale. Researchers have developed relevant methodologies, including the determination of the mechanical characteristics of complex prisms retrofitted with lime-based grouts, as well as on site NDT testing of specific case studies.

4. Conclusions

Lime-based grouts applied for the conservation of historic architectural surfaces, concern a specific repair material category with specialized performance requirements. Their testing usually follows relevant standards, which however focus on different materials (i.e. cement-based grouts, lime-based mortars). As a result, they require adjustments and modifications, as well as a variety of testing results for ensuring their applicability. On the other hand, field testing methods have been developed for assessing the grouts' properties on site.

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Architectural Surface Conservation: Field Testing Techniques for Lime-Based Injection Grouting

1. Introduction

Historic architectural surfaces—such as renders, plasters, mosaics, mural paintings, stone panels, and tiles—are key elements of built heritage, holding significant historical and aesthetic value while protecting underlying structures. Over time, they deteriorate due to environmental exposure and specific loading conditions. Non-structural injection grouting is a common conservation method to stabilize damage such as cracks, voids, deformation, and delamination. As an irreversible conservation treatment, injection grouting must be tailored to existing materials and conditions, requiring thorough diagnostic, implementation, and monitoring strategies[1]. Field tests are considered as essential tools thoroughout this process. They assess surface condition by mapping damage[2-3-4-5] guide grout selection under real-world conditions, ensure their quality during application[6], evaluate the effectiveness of the grouting, and monitor its long-term performance[7].

2. Field test methods for diagnostics and monitoring

Condition assessment of architectural surfaces involves evaluating the affected layers and identifying the location, extent, and severity of damage. Accurate damage diagnosis is essential for selecting appropriate grouts and planning their application. Successive evaluation of grouted areas is important to assess the effectiveness and stability of the intervention, preventing potential failures and costly repairs.

A variety of test methods, from basic to advanced, are used to assess the condition of architectural surfaces and the long-term stability of grouted areas. Tapping is the most common method, relying on the operator's interpretation of sound variations across the surface. Semi-automated acoustic tracing method improves this labour-intensive and subjective method by recording the tapping location and acoustic response, which are analysed to generate defect maps. More advanced acoustic method measures the acoustic energy absorbed when the surface is excited by sound waves, creating acoustic images to map detachments. Laser Speckle Pattern Interferometry measures surface displacements and deformations by analysing changes in laser-generated speckle patterns on the surface due to external excitations. Infrared (IR) thermography detects defects using either passive IR, which relies on natural temperature differences but may be limited in low-contrast conditions, or active IR, which uses external heating or cooling to reveal subsurface issues up to about 10 cm deep. Ground Penetrating Radar (GPR) uses high-frequency electromagnetic waves to detect voids and detachments, but interpreting shallow defects (<8 cm) can be

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2 Rastogi 2001.
3 Calicchia, Bosco Cannelli 2005.
4 Meola et al. 2005.
5 Sklodowski R., Drdacky, Sklodowski M. 2013.
6 Biçer-Şimşir, Rainer 2013 & 2014; Padovnik et al. 2016; Pasian, Martin de Fonjaudran, Rava 2020; Pachta, Papayianni, Spyriliotis 2020.
7 Zendri et al. 2017.

difficult due to signal interference from near-field antenna effects. These field tests require specialized expertise for both execution and data interpretation. Some methods struggle to detect shallow discontinuities, making it necessary to combine techniques. For instance, integrating GPR and IR data using clustering can enhance inspection accuracy.

3. Field tests methods for evaluating performance of grouts

Field tests for evaluating grouts used on historic architectural surfaces are adapted for lime-based injection grouts, similar to laboratory tests, and designed to be simple and easily performed on-site using available tools. Adapted from laboratory methods, they also evaluate key properties, including working properties (e.g., injectability, flow, expansion and bleeding, wet density), properties during setting (e.g., drying shrinkage and final setting time) and hardened properties (e.g., dry density, capillary water absorption, water vapor transmission, bond strength). These tests help identify performance issues by revealing site-specific conditions contributing to problems, guide necessary adjustments, and provide feedback for further laboratory testing. As a quality control measure, they can identify mixing and preparation changes including water content changes and material inconsistencies due to new shipments or storage conditions. While practical and informative, they are less precise than laboratory tests and yield semi-quantitative, site-specific results influenced by environmental and substrate conditions. To ensure reliability, a structured field testing protocol and trained technicians are strongly recommended.

4. Conclusions

Non-structural injection grouting of historic architectural surfaces is a specialized and irreversible intervention that requires a multidisciplinary and methodologically diverse approach. Grouts must be tailored to be compatible with the existing materials and environmental conditions. The grouting process should be guided by a well-structured diagnostic, implementation, and monitoring strategies. Field tests play a vital role throughout all phases of grouting. They help map discontinuities, inform the design and selection of suitable lime-based grouts, and assess application techniques. As a quality control tool, they ensure the consistency and performance of grout. Finally, they support long-term monitoring by verfying the durability and safety of grouted areas over time and enabling early detection of new discontinuities that may compromise the stability of architectural surfaces.

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Special Session

Innovative and sustainable repair mortars and technologies towards resilient restoration of historic buildings – Overview of the SINCERE Project

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Impact of microencapsulated PCMs on lime mortars: thermal and durability assessment

1. Introduction

The durability of construction materials is a critical factor in sustainable building practices, influencing both maintenance requirements and long-term resource utilization[1]. Lime mortars are increasingly favoured over Portland cement-based alternatives due to their lower carbon footprint, recyclability, and carbon sequestration potential, aligning with sustainable construction goals[2]. Incorporating phase change materials (PCMs) into lime mortars enhances their thermal performance, making them more energy efficient. PCMs absorb and release thermal energy during their phase transitions, thereby moderating temperature fluctuations. This ability can decrease the dependency on mechanical heating and cooling systems[3], contributing to energy conservation. Microencapsulated PCMs are especially beneficial in construction applications due to their leakage prevention and stability enhancement of the mortar mix[4]. Additionally, the formulation is optimized with various chemical additives and admixtures to improve the mechanical properties and resistance to environmental stressors of the mortars. This study evaluates the performance of lime mortars integrated with microencapsulated PCMs, aiming to establish them as a viable solution for sustainable, durable, and resilient building materials.

2. Materials and methods

2.1 Materials

The mortars were composed of CL-90-S hydrated calcitic air lime from Cal Industrial S.A., Navarra, Spain, and calcareous sand (0-1 mm) from CTH, Navarra, Spain, with a binder-to-aggregate ratio of 21.7/78.3 by weight. The water content was fixed at 25 wt. % across all mixes. Additives included a superplasticizer (SP, polycarboxylated ether derivative), an adhesion booster (potato starch derivative), and metakaolin (MK, 20% by weight of lime, bwol). SP and starch dosages were adjusted in each formulation to ensure workability and adhesion, as defined in a previous optimisation study[5]. Two types of microencapsulated PCMs with melamine shells and paraffin cores, added at dosages of 5%, 10%, and 20% bwol, featuring melting temperatures of 24°C (PCMT24) and 18°C (PCMT18). A total of 14 mortar compositions were prepared, including reference mixes without PCMs.

2.2 Durability assessment

Durability tests included freeze-thaw and sulfate attack tests. The freeze-thaw test involved 28 cycles of alternating water immersion at room temperature (24h) and freezing at -10°C (24h). For sulfate resist-

1 Cunha, Aguiar, and Ferreira 2017.
2 Manoharan and Umarani 2022.
3 Rubio-Aguinaga et al. 2024.
4 Liu, Wang, and Wu 2019.
5 Rubio-Aguinaga et al. 2024.

Mixture	MK (% bwol)	PCM (% bwol)	SP (% bwol)	Starch (% bwol)
LIME-0	0	0	0.60	0.50
LIME-MK	20	0	0.75	0.50
LIME-TXX/5	0	5	0.75	0.50
LIME-TXX/5-MK	20	5	0.75	0.50
LIME-TXX/10	0	10	0.75	0.50
LIME-TXX/10-MK	20	10	0.75	0.50
LIME-TXX/20	0	20	0.75	0.50
LIME-TXX/20-MK	20	20	0.75	0.50

Table 1. Mix design of laboratory composites. The notation "XX" refers to the type of PCM incorporated (either "24" for PCMT24 or "18" for PCMT18)

ance, specimens were immersed in a saturated $MgSO_4$ solution at 20°C and 95% RH for 24 hours, followed by drying at 110°C, repeating this cycle 28 times with interim rinsing every 10 cycles. For each test, two cylindrical specimens (Ø = 30 mm, h = 40 mm) from each mortar mix were evaluated. After each cycle, these specimens were visually inspected to assess damage progression, following a predefined scale and test protocol described in detail in previous work[6]. Additional characterization tests were performed, including Scanning Electron Microscopy (SEM), hotbox tests for thermal performance, measurements of thermal conductivity, and infrared thermography.

2.3 Cyclic performance

Thermal stability and cyclability were determined through Differential Scanning Calorimetry (DSC), applying forty heating-cooling cycles ranging from -10°C to 50°C at a rate of 20°C/min to evaluate the enthalpy changes associated with the PCM phase transitions.

3. Results and discussion

The study of lime-based mortars incorporating microencapsulated phase change materials (PCMs) and metakaolin (MK) has demonstrated their promising long-term performance, highlighting their potential for sustainable construction. Durability tests, including freeze-thaw and sulfate attack, indicated that mortars with PCMs and MK consistently outperformed the references (Figures 1a-b). The reference mortars exhibited early signs of degradation under cyclic environmental conditions, emphasizing their vulnerability to severe weathering processes. Conversely, the addition of MK greatly enhanced the durability of the mortars, likely due to its pozzolanic reactions that improve the mortar's microstructure. Mortars that integrated both MK and PCMs showed exceptional durability, effectively resisting the detrimental effects of environmental stressors, which underscores the role of PCMs in enhancing the environmental tolerance and extending the lifecycle of these building materials.

Thermal performance assessments through DSC revealed that the PCM-enhanced mortars maintained stable phase transition enthalpies across 40 heating and cooling cycles (Figure 1c, representative of the overall trend). The variability in heat absorption and release was minimal, with a maximum standard deviation of 0.045 J/g across all formulations, which highlights the efficiency and consistency of the PCMs thermal performance Such stability is crucial for their use in energy-efficient buildings, as it ensures reduced reliance on external heating and cooling systems. The highest PCM concentrations yielded the best thermal regulation. Both PCMT24

and PCMT18 mixtures demonstrated excellent repeatability with well-overlapped DSC curves across all cycles, reinforcing their long-term stability. This finding affirms the effectiveness of PCMs in optimizing the energy efficiency of the mortars.

6 Rubio-Aguinaga et al. 2025.

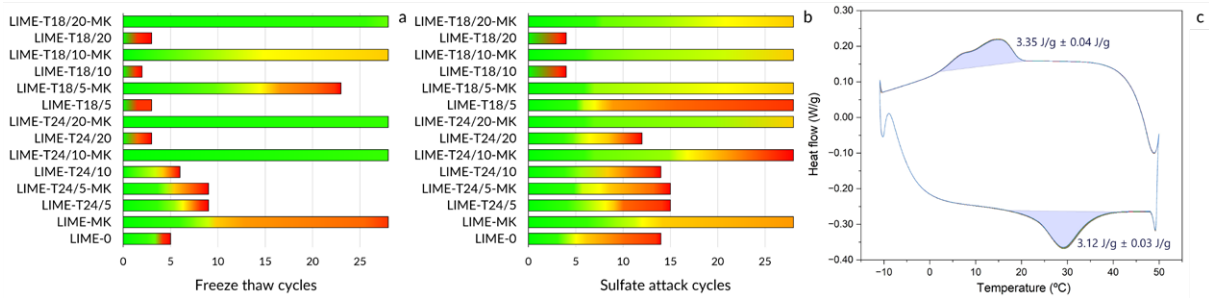

Figure 1. Durability and thermal performance of PCM-enhanced lime mortars. (a) Sulfate attack resistance, (b) Freeze-thaw resistance, (c) DSC cyclic stability of LIME-T24/20 (40 cycles)

4. Conclusions

The evaluation of PCM-enhanced lime-based mortars has confirmed their promising long-term performance, highlighting their suitability for durable and energy-efficient construction applications. The incorporation of metakaolin (MK) substantially enhanced the mortars' resistance to environmental challenges such as freeze-thaw cycles and sulfate attack. Notably, the mortars that combined PCMs and MK displayed the greatest durability. Additionally, the thermal stability and reliability of the PCMs were validated through DSC cyclic tests, which demonstrated consistent phase transition enthalpy over 40 cycles. These results underscore the potential of PCM-lime mortars as optimized solutions for building materials that offer both durability and energy-efficiency, making them an ideal choice for sustainable building practices.

Acknowledgements

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Testing methodologies for self-sensing TRM systems

1. Introduction

It is estimated that 65% of heritage structures is structurally deficient and in critical need of structural and/or seismic retrofitting due to the effects of ageing, climate change and wars. Textile-Reinforced Mortars (TRM), which are externally bonded composite systems comprising inorganic matrices reinforced with advanced fibre meshes, are already regarded as an effective strengthening solution for heritage structures. They offer high strength and ductility whilst ensuring minimal invasiveness and excellent compatibility with historic substrates . However, the low resistance to cracking of the mortar under service conditions has the potential to affect long-term performance, potentially resulting in additional repairs and costs, as well as critical safety issues. With the aim to integrate structural health monitoring technologies to ensure timely intervention, while drawing inspiration from recent advances in self-sensing materials, TRM are ideal candidates to be transformed into multi-functional systems, as both textile and mortar can be used as sensory elements through appropriate functionalisation. Despite the tremendous potential, literature is still in its infancy and solutions are limited to the use of carbon or hybrid glass/carbon textiles, where carbon yarns act as sensory element, providing nonetheless encouraging evidence that changes in the electrical impedance can be well correlated to the TRM structural state.

2. Materials and Experimental Programme

A series of eight direct tensile tests were performed on TRM composites, with dimensions of 500x50x10 mm3, in accordance with ACI549.6R, with concurrent monitoring of the change of the electrical resistance under monotonic loading up to rupture (Figure 1). Lime-based mortars were reinforced with short dispersed recycled carbon fibres and combined with a bidirectional glass textile. Different electrical acquisition protocols were adopted: The electrical measurements were obtained using the four-wire method, with sensors either embedded within the composite in the form of wires or externally bonded on the composite using copper tapes in different configurations. The sensitivity obtained with alternate (AC) or direct (DC) current excitation on the detection of crack formation during loading was also assessed, correlating the electrical data with cracks evolution obtained through Digital Image Correlation.

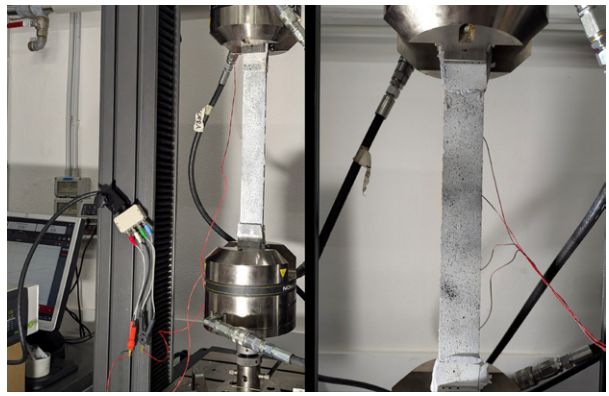

Figure 1. Test setup for the electro-mechanical characterisation of TRM coupons in tension.

3. Preliminary Results

From the analysis of the preliminary results, it was determined that the highest degree of correlation between the fractional change of electrical resistance and crack formation was obtained in the TRM specimens with electrodes attached on the transverse yarns of the glass textile under DC injection. Specimens with both two and four electrodes resulted in excellent monitoring performance, with the latter able to capture the individual cracks and identify their position along the specimen due to the more distributed location of the electrodes (Figure 2). Conversely, electrical data acquisition through copper tapes applied on the mortar was proven to result in poor sensing capability, possibly due to the lack of a good electrical connection at the electrode/mortar interface as well as the presence of the non-conductive glass textile, which captures the injected current.

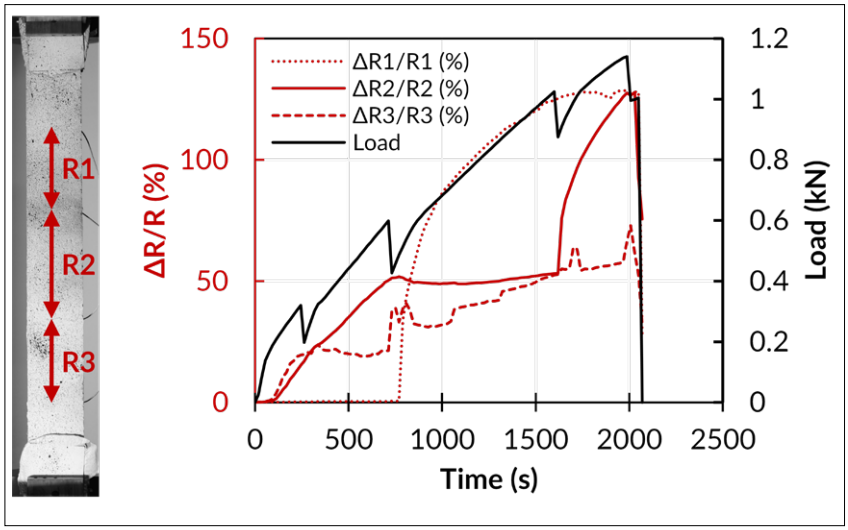

Figure 2. Change of electrical resistance and load application versus time.

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The Durability of Vaterite Calcined Clay Repairing Mortars: Another Sustainability Aspect in Innovative Low-CO2 Materials

1. Introduction

The construction industry significantly contributes to global CO_2 emissions, with cement production alone accounting for approximately 8% of total anthropogenic carbon dioxide emissions1. Addressing this environmental challenge requires strategies that both reduce emissions during material production and extend the lifespan of structures through enhanced durability. Developing low-carbon cementitious binders is thus essential to achieving sustainable construction practices1. Limestone Calcined Clay Cement (LC3), capable of replacing up to 50% of Ordinary Portland Cement (OPC) has emerged as a promising solution[1]. More recently, Vaterite Calcined Clay Cement (VC3), which substitutes calcite with vaterite, a metastable polymorph of calcium carbonate, has gained attention due to its potentially superior mechanical and microstructural properties attributed to vaterite's increased reactivity[2].

In addition to adopting environmentally friendly materials, sustainable construction can benefit significantly from restoring and repurposing existing buildings. Many structures requiring renovation, often constructed less than a century ago using traditional concrete and cement-based materials, hold substantial cultural or social heritage value. Integrating low-carbon materials into renovation practices can thus harmonize environmental sustainability with heritage preservation. Selecting an appropriate cementitious binder is crucial for ensuring the long-term durability and effectiveness of restoration interventions. Although LC3 has been extensively studied, VC3 remains relatively unexplored, particularly in terms of durability[3]. Previous studies indicate that incorporating vaterite enhances workability and compressive strength, suggesting that VC3 could offer a suitable alternative with performance advantages and a lower CO2 footprint. However, crucial durability parameters, such as permeability and sulfate resistance, remain largely unknown. Evaluating these factors is vital to establish VC3's viability as a sustainable cement alternative.

This study aims to address this knowledge gap by investigating VC3's durability relative to LC3 and OPC. Experimental mortar samples were prepared, including a reference OPC mortar and mortars where calcite was progressively replaced by vaterite at increments of 0%, 5%, 10%, and 15%. The materials' performance was evaluated based on key parameters: mechanical strength, capillary water absorption, and sulfate resistance. This comprehensive evaluation provides insights into the long-term behavior of VC3, contributing valuable data towards advancing sustainable cement technologies and addressing both environmental and structural challenges.

1 Zunino, and Scrivener 2021.
2 Li et al. 2024.
3 Nofalah et al. 2024.

2. Materials and Methods

2.1 Materials and mix designs

This study utilized commercial CEM I 52.5 R cement (CE and NF certified) sourced from Grupo Cementos Portland Valderrivas. Metaver N metakaolin (MK) was obtained from NEWCHEM, while calcium carbonate (Calcite) CACB-00A (>99% purity) and gypsum CASU-02A (>99% purity) were supplied by Labkem. CEN Standard Sand conforming to EN 196-1[4] specifications was also used. Vaterite was synthesized via a precipitation method detailed in prior research.

Five different repair mortar mixtures were prepared, maintaining consistent proportions to ensure comparability. All mixtures were prepared with a fixed water-to-binder ratio (w/b) of 0.5 and a sand-to-cement ratio by weight of 3:1. Mix design details are presented in Table 1. After preparation, cylindrical specimens (Ø = 30 mm, h = 40 mm) were subjected to mechanical and durability testing as described below.

2.2 Methods

The compressive strength (CS) of cylindrical mortar specimens was measured after curing periods of 28 and 91 days, in compliance with ASTM C39[5]. For the sulfate attack durability test, specimens were immersed in a saturated $MgSO_4$ solution at 20°C and 95% RH for 24 hours, followed by drying at 110°C, repeating this cycle 21 times. Three cylindrical specimens from each mortar mix were evaluated[6]. The results are presented in Table 1 and Figure 1.

Mixture	Cement (%)	MK (%)	Gypsum (%)	Vaterite (%)	Calcite (%)	CS 28 days (Mpa)	CS 91 days (Mpa)	Capillary absorption coefficient (kg/(m2·s0.5))	WL (%)
T1 (Control)	100	0	0	0	0	30	30,1	0,25	0,2
T2	50	30	5	0	15	18,9	23	0,22	9,6
T3	50	30	5	5	10	20,7	25,9	0,23	9,7
T4	50	30	5	10	5	23,1	28,4	0,22	7,2
T5	50	30	5	15	0	24,7	29,8	0,21	5,7

Table 1. Mix design of mortars, compressive strength and durability test results. CS: Compressive Strength, WL: Weight loss after 21 cycles

3. Materials and Methods

The compressive strength results indicate that long-term strength (28–91 days) generally improved with increasing vaterite content, with the T5 mixture exhibiting the highest performance. At 28 days, the compressive strength of Calcite- and Vaterite-based materials ranged from 60% to 80% of OPC mortar strength. By 91 days, these alternative mortars achieved between 75% and 99% of OPC strength, demonstrating notable improvement.

Capillary absorption test indicated that the control mortar exhibited the highest absorption coefficient, whereas calcite-based mortar showed greater absorption compared to mortars containing vaterite. Additionally, increasing the vaterite content progressively reduced the absorption rate.

Weight loss (WL) measurements from the sulfate salt attack test highlight enhanced durability in mortars containing higher proportions of vaterite. Samples with increased vaterite content experienced less weight loss compared to those with higher calcite content. Notably, the control sample remained undamaged throughout the testing, exhibiting no recorded weight loss. Figure 1 presents the specimens' visual condition before the first cycle and after the completion of the final cycle.

4 UNE-EN 196-1:2018.
5 ASTM C39/C39M:(2016).
6 UNE-EN 772-11:2011.

Figure 1. Specimen's condition before and after salt attack durability test: (a) T1; (b) T2; (c) T3; (d) T4; (e) T5. Top row: Samples before first cycle, Bottom row: Samples after the completion of the test. Each photo represents the average state of each mixture.

4. Conclusions

This study demonstrates that increasing vaterite content in calcined clay cement enhances long-term compressive strength, reduces capillary absorption, and improves sulfate resistance. The T5 mixture exhibited the best overall performance, achieving up to 99% of OPC strength at 91 days. Higher vaterite proportions also resulted in lower weight loss during sulfate exposure, indicating superior durability. These findings highlight VC3 as a promising low-carbon binder suitable for sustainable construction and heritage restoration. Further research should investigate additional durability aspects to fully validate its practical applicability in real-world scenarios.

Acknowledgments

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Lime-based Mortars for Thermal Retrofitting of Historic Buildings – Key Challenges for Field Application

1. Introduction

Enhancing energy efficiency in historic buildings within cultural heritage conservation presents complex challenges. These structures require minimal intervention to preserve their historical and architectural integrity, yet they must also meet modern energy standards. The SINCERE project addresses this by developing advanced lime-based mortars incorporating Phase Change Materials (PCMs) and natural hemp fibers, tailored to improve thermal performance without compromising reversibility, compatibility, or non-detrimentality.

Historic buildings, often poorly insulated, represent a significant part of urban heritage. Retrofitting these with energy-efficient solutions not only reduces global energy consumption but also ensures their ongoing usability. The use of PCMs and hemp in lime mortars offers a promising approach to stabilize indoor temperatures and enhance insulation[1-2], without the need for extensive mechanical heating or cooling systems[3], while also contributing to carbon sequestration—vital in combating climate change[4].

This research supports the broader goal of integrating innovative building materials into heritage conservation strategies, ensuring that interventions are compatible to the original fabric of historic buildings and do not accelerate substrate degradation or disrupt historical aesthetics.

2. Materials and Methods

The research involved developing two distinct groups of formulations to enhance the thermal efficiency of heritage buildings. For the PCM-enhanced mortars, a variety of PCMs was utilized, distinguished by different melting temperatures to cater to diverse climatic conditions and thermal management requirements. These PCMs included both microencapsulated types, which are ideal for their ability to contain phase change materials without leakage during the phase transition, and silica-supported types, which provide added stability and lower cost. This selection was strategic to explore the efficacy of different PCM formulations in stabilizing indoor temperatures through their heat absorption and release capabilities.

The testing protocol for these PCM-enhanced mortars was extensive and included rigorous mechanical testing to ensure the mortars met structural requirements without causing damage to existing substrates. Thermal performance was assessed using a range of techniques including thermal conductivity tests, and hot-box simulations. Although not included in this abstract, these methods supported ongoing investigations on insulation performance and thermal buffering capacity. In addition, both the PCM-enhanced mortars and hemp-based mortars were applied to hempcrete blocks to evaluate adhesion qualities and to visually observe any occurrences of cracking or other defects.

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1 Theodoridou, Kyriakou, Ioannou 2016, 539-545.
2 Agliata et al. 2020, 4620.
3 Rubio-Aguinaga et al. 2024, 138862.
4 Parcesepe et al. 2021, 882.

Parallel to this, hemp-based mortars were developed to leverage the insulating properties and environmental benefits of hemp. These mortars were subjected to compression tests to evaluate their mechanical strength, setting process tests to assess how the mortar hardened, and plaster application examinations to ensure that the mortar could be applied effectively and performed well as a plaster. This included tests for adhesion and visual observations to assess the integrity and effectiveness of the mortar when applied to hempcrete blocks.

3. Results and Discussion

The comprehensive evaluation of both PCM-enhanced mortars and hemp-based mortars revealed varied impacts on their performance. Fresh state properties and qualitative assessments on hempcrete block substrates showed positive outcomes for PCM-enhanced mortars, highlighting their compatibility and effectiveness in practical applications.

3.1 Fresh State Properties and Qualitative Evaluation

All mortar mixtures, as seen in Figure 1a-e, exhibited satisfactory adhesion to the hempcrete substrate, with no visible signs of detachment, cracking, or shrinkage. This indicates good compatibility of both PCM-enhanced and hemp-based mortars with the hempcrete surface, which is crucial for their potential application in real-world restoration and retrofitting projects.

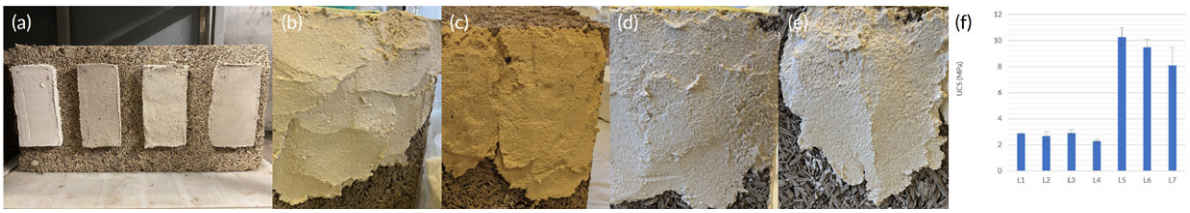

Figure 1. Mortar application on hempcrete blocks: (a) PCM-enhanced mortars; (b-e) hemp-based mortars. (f) Compressive strength at 28 days of PCM-enhanced composites

3.2 Compressive Strength

Compressive strength tests displayed significant variability dependent on the type of PCM used as seen in Figure 1f. Mortars with silica-supported PCMs (L5-L7) at 28 days of curing showed higher strengths, achieving a maximum of 10.28 MPa. In contrast, slurry-based microencapsulated PCM mortars (L2-L4) maintained compressive strength levels comparable to the reference mix (L1), with strengths ranging from 2.29 to 2.91 MPa. The strength variations observed reflect the influence of different additives: silica-supported PCMs contributed to improved mechanical resistance due to their inorganic matrix and particle stability, while microencapsulated slurry PCMs maintained comparable strength to the control mix. Conversely, hemp inclusion reduced strength, consistent with the fibrous and less dense character of the additive. Furthermore, mixes with metakaolin substitution exhibited improved performance, whereas natural pozzolan reduced mechanical properties, particularly at higher cement replacement levels.

3.3 Setting Process and Plaster Application and Thermal Assessment

Hemp mortars exhibited longer setting times, especially with high NP content, complicating application in practical settings. However, optimized mixes achieved suitable workability and setting times, ensuring they could be effectively applied as plasters. During application tests, these mortars adhered well to hempcrete blocks, with procedures adjusted to minimize water absorption and ensure robust application without premature drying or cracking.

These results reveal the complex interactions between material compositions, environmental conditions, and application techniques, emphasizing the need for tailored mix designs that balance sustainability, functionality, and compatibility with heritage conservation principles.Preliminary thermal assessments

indicate that the use of PCM-enhanced mortars can reduce indoor temperature fluctuations by up to 3–4°C, depending on the PCM type and climatic conditions, suggesting a meaningful potential for reducing heating and cooling demands in historic structures.

4. Conclusions

The research has significantly advanced the retrofitting of heritage buildings with sustainable, efficient materials. PCM-enhanced mortars, utilizing a variety of phase change materials, effectively stabilized indoor temperatures, thereby reducing reliance on mechanical climate control systems. These mortars, including both silica-supported and microencapsulated types, met mechanical and thermal performance benchmarks, showed excellent adhesion, and exhibited minimal cracking on hempcrete blocks, demonstrating their potential for integration into existing structures.

Hemp-based mortars leveraged the natural insulating properties of hemp, enhancing the sustainability of retrofitting practices. Despite a reduction in mechanical strength, these mortars performed well as plasters in terms of adhesion and structural integrity during setting, making them viable for real-world applications.

Future research will focus on scaling these materials for larger applications, enhancing their long-term durability, and optimizing formulations to meet broader sustainability and compatibility goals. This continued development is crucial for aligning heritage conservation with modern environmental objectives.

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Durability and compatibility requirements of repair mortars for structural retrofitting of 20th-century built heritage

1. Introduction

The structural retrofitting of 20th-century built heritage presents unique challenges due to the materials and construction techniques used during this period. Reinforced concrete and masonry became dominant, requiring specific approaches for repair and restoration. One of the key concerns is the selection of appropriate repair mortars to ensure both durability and compatibility with the original structure. Inappropriate choices can lead to early degradation, mechanical instability, and loss of historical authenticity. Proposed research focuses on the durability and compatibility requirements of repair mortars for the structural retrofitting of 20th-century built heritage, ensuring material selection, performance assessment, and long-term durability.

2. Challenges in repair and retrofitting of 20th century heritage buildings

Unlike older historical structures primarily built with stone and lime mortars, 20th-century heritage buildings mostly incorporate cement-based materials such as reinforced concrete or mortar-bound masonry. These materials pose distinct challenges:

Material aging and degradation: reinforced concrete and masonry structures suffer from carbonation, chloride-induced corrosion, and alkali-silica reactions, affecting their structural integrity.

Compatibility with original materials: the repair mortar must match the mechanical and chemical properties of the existing structure to prevent stress concentrations, differential shrinkage, or moisture entrapment.

Durability in aggressive environments: many 20th-century buildings are exposed to urban pollution or aggressive chemical environment, requiring mortars with enhanced resistance.

2.1 Compatibility

The selection of repair mortars must ensure compatibility in the following aspects:

Mechanical compatibility: the repair mortar should have a modulus of elasticity, strength, and adhesion similar to the substrate to avoid stress concentrations and cracking.

Chemical compatibility: alkali content, sulphate resistance, and reactivity with aggregates must be considered to prevent detrimental interactions.

Moisture and permeability compatibility: mortars should allow appropriate vapor permeability to prevent moisture entrapment, which could accelerate deterioration.

Advanced approaches, such as the use of modified reinforced cement-based mortars and low-clinker mixes are being explored to address these compatibility concerns.

2.2. Durability

For long-term efficiency, repair mortars must meet strict durability requirements:

Sulfate and chloride resistance: essential for structures exposed to salts, marine environments, or polluted urban settings.

Carbonation resistance: essential for reinforced concrete buildings to mitigate steel reinforcement corrosion.
Shrinkage control: low shrinkage properties minimize the risk of cracking and debonding over time.
Recent advancements in fiber-reinforced mortars, self-healing materials and corrosion-inhibiting materials offer promising solutions to enhance the performance.

3. Case studies and practical applications

Several case studies will illustrate the successful application of durable and compatible repair mortars in 20th-century built heritage retrofitting, in the context of the SINCERE Horizon Europe Project in different regions.

4. Conclusion

The durability and compatibility of repair mortars are critical factors in the successful retrofitting of 20th-century heritage buildings. Besides the balance between compatibility and long-term durability considerations, it is essential to ensure the sustainability of repair interventions. Emerging technologies, such as fiber reinforcement, PCMs and self-healing materials, present promising opportunities for future research and applications. A multidisciplinary approach involving materials science, conservation principles, and structural engineering is needed to develop optimized repair solutions that respect the heritage value while ensuring long-term performance.
This research underscores the need for site-adapted material selection for the effective preservation and retrofitting of 20th-century heritage buildings.

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Building for the people - the role of citizen science for the preservation of built heritage

1. Building for the people

The preservation of built heritage is a complex issue. First, cultural heritage is a moving target, and authenticity is by itself a challenging question since there are many "layers" of heritage; and time itself is a part of it. Things become more complicated when built heritage is put into actual use. In this case, modern requirements for safety, comfort, and low costs, among others, come often in direct tension with the requirements for preservation. Adding on top the urgent need for sustainable construction and low energy consumption, there are direct effects on aesthetics, maintenance, and renovation costs. Such a complex problem cannot have a purely engineering solution and thus the role of the public at all stages of the process becomes critical. First, people have memories and personal perspectives on the heritage value of buildings. In fact, architectural heritage buildings are significant parameters of peoples own cultural identity as well as self and place awareness. Second, the local community has specific needs and constraints regarding the activation of abandoned buildings, and their usage. Third, the building's users are the most important piece for their maintenance, and the realization of the potential of sustainable building technologies, for example through informed monitoring of the built environment and the proper usage of the building. Finally, the people are those that will be affected by the additional costs, and they need to understand the value of the additional investments on time and money required.

2. Citizen science

Citizen science in cultural heritage has evolved into a diverse field where citizen engagement varies from passive data collection to active decision making in reuse and preservation. Many projects develop specialized digital platforms to involve citizens in documenting, mapping, and analyzing cultural assets. Crowdsourcing initiatives like Micropasts and Europeana Transcribe, engage volunteers in transcribing historical records. More immersive projects encourage residents to share oral histories, monitor building conditions or even test restoration techniques in participatory living labs. This range of engagement, from contributory (e.g., data collection) to co-creative (i.e., collaborative research and decision making), demonstrates the increasing role of citizens not just as observers, but as active participants in shaping the cultural heritage science and narrative. Most participatory heritage projects prioritize data collection, mapping, and storytelling, while technical aspects of conservation, such as materials, eco-friendly renovation techniques, or energy efficiency in heritage buildings, tend to remain within expert-driven domains. A possible reason is that material science, structural restoration, and energy optimization require technical expertise, making it harder to involve citizens in a meaningful way. Moreover, unlike photographing a historic site or transcribing old texts, testing materials or energy solutions often requires lab-based analysis, specialized tools, and controlled environments. Finally, conservation and renovation of heritage buildings are often tightly regulated, limiting public experimentation with materials or interventions.

3. The Talking Buildings Game

The SINCERE project, https://sincere-project.eu/, develops innovative renovation materials and technologies, experimenting with a wide range of low CO2 restoration mortars trying to balance a set of trade-offs regarding their thermal conductivity, compressive strength, cost, permeability, reversibility, recyclability, workability, and self-healing capacity, among others. Although finding the right balance between all these qualities is at its core a technical task, making the final decisions on the right combination of materials to be applied for a specific renovation project highly depends on the local context and the role of citizen participation in the process can be very useful. To meaningfully engage citizens in such a complex task, the SINCERE project introduces an innovative citizen science methodology, the Talking Buildings Game, a process of incremental engagement with a building based on the idea of impersonation of non-human entities, drawing inspiration from Bruno Latour's Actor-Network-Theory[1].

Asking a group of people living or working in a cultural heritage building (e.g., the students at a university) to observe it, to frame and to connect to a certain part of it, and then to tell a story from the perspective of this object or collection of objects, by impersonating them, is a comprehensive list of instructions, what we call the Talking Buildings Game. This generic "challenge" can then be refined with the contributions of researchers to direct the attention and the outcomes of the process toward specific research questions, learning objectives, and maintenance tasks. There are infinite variations of the Talking Buildings Game, and in this article we report on three concrete examples initiated in the context of the SINCERE project, which will provide very rich material for comparisons and refinement of the game, toward the construction of a toolkit.

In Rhodes the citizen science process took the form of an open campaign, and then it will be further elaborated to target pupils and staff of primary school and higher education hosted in cultural heritage buildings, like various schools in Rhodes that are listed as monuments. At the first stage of the game, the open challenge, the campaign was initiated through the very popular local radio station Radio Lihnari, in combination with social media. Participation in the Talking Buildings Game involves various options of giving a voice to a building through digitalised art forms such as: audio clips, short video clips, photos with captions and short scripts of creative writing. In Israel, students of a design school (the Holon Institute of Technology) are trained in the impersonation methodology which they are asked to use in design workshops taking place in different places and in collaboration with students from other academic institutions, like the "The spirit of material: Building sustainability" workshop in Xanthi, and a forthcoming workshop in the context of the Design Month Graz. Inviting the students to reflect on this experience of impersonation reveals many interesting aspects of the process and its valuable input for researchers and experts. Finally, in Ostrava, Czechia, we will follow a "bottom-up" approach, starting from the technical perspective, which will be introduced from the very first steps of the game with the organization of a series of workshops titled "the eyes of the expert". These workshops will first train citizens to observe buildings as engineers and architects do, and thus expand their knowledge and imagination, before engaging with the Talking Buildings Game.

From the two first processes already started the first results are very encouraging. Impersonation is both entertaining and engaging, and it has a great potential to increase citizen's literacy about the built environment and empower them to become part of the solution of complex restoration and maintenance processes.

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HBIM and BEM driven design and selection of repair mortars for enhancing energy performance of historic buildings under climate change

1. Aims and Objectives

Historic and cultural heritage buildings are the trademark of numerous European cities, towns and villages. They form the EU Built Cultural Heritage (BCH), a living symbol of Europe's rich historical and cultural background, reflecting and shaping the identity of our local, national and multinational societies. However, recent studies indicate that 40% of the total energy consumption in the EU is consumed by buildings (35% worldwide). Historic buildings make up 30% of the European building stock and account for more than a third of the total energy consumption in the residential sector across the EU, with 35% of them over 50 years old and 75% inefficient in their use of energy[1].

Considering the paramount stock of historic buildings in the EU, the advantages provided by novel multifunctional conservation mortars are essential, in order to enable sustainable re-use and refurbishment of BCH including 20th century buildings and achieve sustainable development goals and priorities set by EU. In fact, conservation, renovation and rehabilitation of existing buildings represents more than 17% of the saving potential of the EU economy up to 2050, lowering CO2 emissions by about 5%[2]. Despite the raising attention of the European Green Deal, the green transition of Architectural/Built Heritage is still lacking[3]. Moreover, climate change plays an important role on the levels of energy consumption and energy requirements during the use of historic buildings and is becoming a crucial parameter when assessing the building performance.

This study aims to address the data-driven decision making and materials selection for the thermal retrofitting of historic buildings, both at material/mortars scale and building/structure scale, through the use of Building Information Modeling (BIM) and Building Energy Modelling (BEM) tools.

2. Methodology

Different prediction tools have been used to forecast future climate scenarios due to climate change (based on the Intergovernmental Panel on Climate Change (IPCC) projections) and have been incorporated in the energy needs scenarios parameters used for evaluating the efficiency of the thermal retrofitting mortars proposed.

The energy enhancement scenario was implemented in a school building, a neoclassical structure in the Medieval Town of Rhodes (Figure 1), built at the end of the 19th century, for evaluating the impact of two types of thermal retrofitting mortars. The school is a single-story building which experiences a hot-summer Mediterranean climate (Csa) characterized by hot, dry summers and mild, wet winters. The two types of mortars used are: i) lime-based ternary mixtures with microencapsulated phase-change materials and ii) lime-based mortars with vegetable fibres. The interventions that have been examined include: (S1)

1 EU-Energy performance of buildings. https://ec.europa.eu/energy/en/topics/energyefficiency/buildings.
2 Economidou et al. 2011.
3 EU OMC Expert Group of Member States in its report on "Strengthening cultural heritage resilience for climate change", 2022.

application of repair mortars with PCMs in the external walls and (S2) repair mortars with hemp in the external walls.
Differential Scanning Calorimetry (DSC) was conducted for characterizing enthalpy of PCMs (J/g) during melting/freezing cycles, as well as thermal conductivity measurements for characterizing the thermal retrofitting mortars. These measurements were used as modelling input in EnergyPlus software for running simulation models[4]. The scenario implemented in the school building has calculated the electricity consumption across different environmental conditions, assuming energy consumption for cooling, heating, lighting, and electrical equipment.

3. Results and discussion

The HBIM-based workflow has been used for supporting the preliminary design of energy retrofit interventions on the presented case study. In particular, the envelope system was investigated as its improvement is considered essential for reducing the energy consumption and CO2 emissions during the operation and maintenance phases. The workflow consists of three main phases: a) the building documentation phase (architectural, historic, engineering and conservation surveys), b) the computational phase that includes the realization of the HBIM Model and the Building Energy Model (BEM), and c) the predictive phase, where energy interventions needs and material/intervention costs are calculated through BIM, while benefits during the lifecycle have been predicted through BEM in terms of thermal demand and energy costs for heating data.
The building in Rhodes, Greece, exhibited notable energy savings after applying the PCM-mortars. Implementing different repair mortar strategies has resulted significant reduction of energy use, achieving savings between 30-50%. These values have been attributed primarily to the reductions in heating demand. The overall results highlight substantial efficiency gains in both cooling and heating energy use, confirming the effectiveness of PCM-enhanced mortar in improving thermal performance, particularly in a Mediterranean climate.
The selection of PCM-mortars for thermal retrofitting of the historic buildings in a climatic zone similar to Rhodes' climate, seems very effective since hot summers provide ample opportunities for PCM to absorb excess heat and reduce cooling demands, while mild winters allow for partial heat release.
Overall, the multi-criteria analysis implemented in this work allowed the comparison of different intervention combinations (in terms of mortars composition and application parameters), indicating the optimal solution for the energy improvement of the building, taking into consideration technical, economic, energy, and environmental issues.

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4 Lygerakis et al. 2024.

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Pozzolanic mortars, properties and formulations for the restoration of Helsinki Cathedral

1. Introduction

In architectural restoration, it is crucial to ensure the compatibility and affinity of new materials with the originals to avoid risks associated with differential behavior over time[1]. In this context, pozzolanic mortars represent an ideal solution: obtained from the combination of aerial lime and reactive silica-aluminous materials (pozzolans), they have hydraulic properties that make them suitable for use in damp environments or exposed to atmospheric agents[2]. Such mortars are distinguished by their durability, compatibility with traditional materials, and versatility, which allows the formulation of ad hoc mixtures according to the specific needs of the site or the historical-architectural context.

In the present study, two single-layer mortars were formulated and tested for the restoration of the exterior surfaces of Helsinki Cathedral, a neoclassical building dating from 1852. The objective is to corroborate the durability of pozzolanic mortars exposed to severe climatic conditions, while meeting demands for material, aesthetic, and performance compatibility.

2. Materials and methods

2.1 Materials

For conservation work at Helsinki Cathedral, two specific plaster formulas referred to as Rasosasso Monostrato A and Rasosasso Monostrato B were developed, specially formulated for the integration and reconstruction of thick historic plasters.

The basic plaster composition is comprised of pozzolanic hydraulic lime and 0-3 mm calcareous-siliceous sand, but the two formulations differ in the relative percentage of aerial lime, pozzolans, and aggregate, and are optimized to achieve different characteristics, both in terms of performance in adhesion and mechanical strength, and aesthetic compatibility. Both plasters were applied to samples consisting of historic solid brick (size 12 × 25 × 5.5 cm), characterized by a higher intrinsic salinity than that of the real substrate and therefore are considered worse material in terms of mechanical properties for subsequent material tests. This choice made it possible to evaluate the performance of the plasters under conditions of high stress, simulating more severe potential degradation scenarios than the real conditions.

2.2 Methods

The samples were subjected to an accelerated aging cycle at Eurac Research's Accelerated Life Testing Lab and Hygrothermal Testing Lab, with the purpose of evaluating the durability of the materials under extreme environmental conditions. In the first phase, the samples were exposed to neutral salt spray at 35 °C for 5 days. Then, they were wetted according to a procedure defined by hygrothermal simulations in dynamic regime conducted with WUFI Pro software; the simulations aimed to estimate the typical

1 Charta del Restauro di Roma 1883.
2 Charta del Restauro di Roma 1883.

moisture content of a plaster exposed to the climate of the city of Helsinki. Finally, the specimens were subjected to freeze-thaw cycles for five days, with a temperature range of 10°C to -30°C.
After the treatments, all samples were dried completely and subjected to comparative analysis at the Calchèra San Giorgio laboratory to compare the performance of the aged specimens with the untreated ones. In addition to compressive strength (UNI EN 1015-11) and adhesion to substrate (UNI EN 1015-12), contact angle measurement (UNI EN 828) was performed to assess changes in surface water repellency as a result of aging. Finally, a visual assessment of color changes was conducted through direct observation and qualitative comparison between treated and untreated samples to detect any changes in surface appearance.

3. Results and discussions

The tests evaluated the durability and physical-mechanical performance of two plasters developed for Helsinki Cathedral under accelerated stress conditions.
Both mortars exhibited stable values of compressive strength and adhesion, as well as good surface cohesion, even after stress cycles. Compressive strength increased, particularly for Rasosasso Monolayer A, as expected in pozzolanic materials, which improve performance over time. Adhesion remained essentially unchanged. The contact angle showed a slight increase in wettability on all samples after treatment. The materials also effectively limited the migration and crystallization of salts from both the substrate and the surface. Efflorescence was concentrated primarily at the brick-plaster junction, a boundary condition not representative of in-situ behavior, because the bricks are fully coated there.

Figure 1. Samples arranged inside the salt spray test chamber.

Campione	Resistenza compressione 120 gg (MPa)		Aderenza (MPa)		Angolo di contatto		Alterazioni visive
	prima	dopo	prima	dopo	prima	dopo	dopo
Monostrato A	7.23	10.91	≥ 0.5	≥ 0.5	70,74°	49,41°	nessuna
Monostrato B	6.93	7.83	≥ 0.5	≥ 0.5	68,46°	42,81°	disuniformità cromatica lieve

Table 1. Sample results before and after accelerated durability tests.

4. Conclusion

After accelerated stress tests, Rasosasso Monostrato A proved to be the best performing, providing excellent mechanical durability, surface cohesion, and resistance to salt degradation.
The results also confirmed the high quality of pozzolanic lime mortars, which proved to be particularly effective in ensuring stable performance, even under extreme environmental conditions without showing significant degradation phenomena.

These outcomes confirm their suitability for the restoration of historic buildings located in severe climatic contexts, such as in Helsinki. Future prospects include adapting the formulations to different media and environmental conditions, with the goal of extending their use to other critical conservation contexts.

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MASSIMILIANO MAGAGNOLI

Building according to tradition

Biocalce is a range of natural hydraulic lime mortars by Kerakoll, produced in the traditional way by firing pure marly limestones in vertical kilns at approx. 800 – 1,000 °C.
The lime firing process (calcination), without the addition of clay or other corrective raw materials, influences the physical and mechanical characteristics of the resulting natural lime, guaranteeing natural hydraulic properties and hardening with water, and a gradual improvement over time due to how it reacts with CO2.
The purity of the raw material and the low-temperature firing process, followed by a long period of slaking and maturing, guarantee a quality product certified in compliance with the en 459-1 (NHL) standard.

1. Biocalce: the plaster that lasts

1.1 Durability and resistance
Biocalce plaster guarantees excellent durability and resistance to humidity and deterioration, in both indoor and outdoor environments. This makes it ideal for historical restoration and sustainable architecture. Thanks to its pozzolanic properties and the slow carbonatation of the lime, mechanic and chemical resistance improve over time without harmful stress. In addition, the formula ensures excellent adaptability to existing masonry and high resistance to destructive salts.
Biocalce guarantees the absence of chemical reactivity in the presence of salts and excellent durability of the plasterwork.

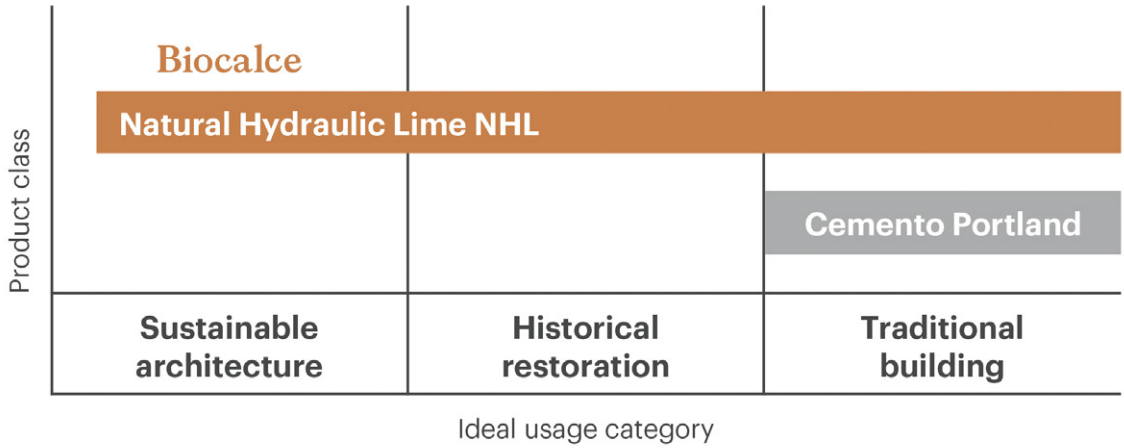

Figure 1. The NHL (natural ydraulic lime) is the ideal binder for any type of building

Biocalce recovers and renews the roman building tradition. For more than 2,000 years, the lime/pozzolan duo has been synonymous with durability and well-being.

2. Biocalce, a complete range for modern buildings, sustainable architecture and historical restoration

The products Biocalce Intonaco, Biocalce Rinzaffo and Biocalce Zoccolatura have WTA certification. WTA (Wissenschaftlich-Technische Arbeitsgemeinschaft fur bauwerkserhaltung und denkmalpflege e.v.) is the international association for science and technology of building maintenance and monuments preservation, and WTA certification is a quality mark that guarantees the reliability and efficacy of the materials and methods used in restoration. The process involves the development of guidelines, independent testing of products, and the awarding of the certification to those products that meet WTA standards.

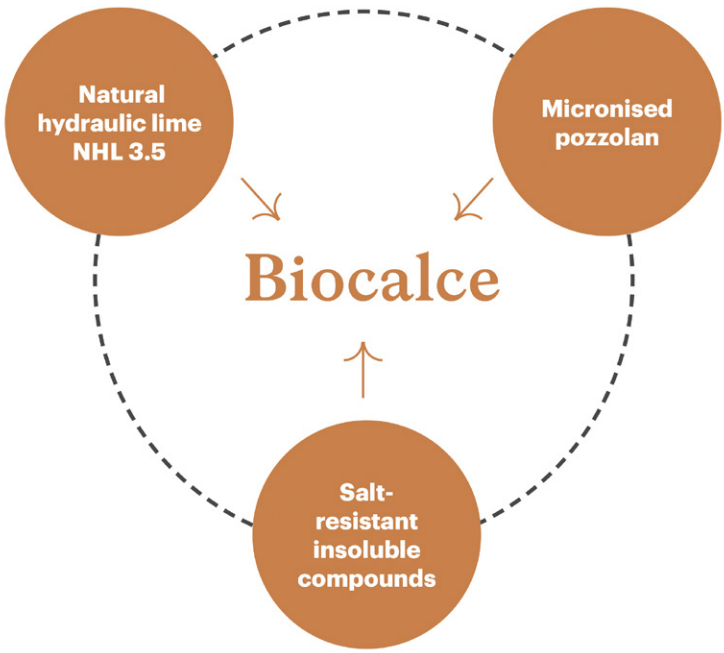

Figure 2. The association between lime and pozzolan creates a salt resistant mixture

3. Restoration and structural reinforcement: innovation in keeping with tradition

Protecting existing buildings offers a strategic opportunity to preserve the historical and architectural identity of an area. In this context, systems for structural reinforcement using inorganic matrix composites are a cutting-edge solution that is particularly effective for the consolidation of historical masonry.
The use of the NHL 3.5 hydraulic lime mortars in the Biocalce range, in synergy with the products from the Geocalce range, meets the essential requirements for work on historical buildings: chemical and physical compatibility, breathability, reversibility and respect for the authenticity of the original materials.
In the restoration of monuments, the aim is to restore the original integrity of the architectural elements, with specifically dedicated repair and reintegration operations. The use of lime as a binder is the option most consistent with traditional construction techniques, guaranteeing mechanical compatibility and reversibility. This approach is in stark contrast to systems based on polymer-modified cement mortars or epoxy resins, which are often incompatible with historical supports.
Following the seismic events of recent decades, numerous operations on listed buildings – including churches and monuments – have been carried out using the certified Geosteel SRG and FRCM systems. These technologies, based on the use of mortars from the Geocalce Antisismico range, combined with

geosteel g unidirectional steel sheets or geosteel grid basalt fibre mesh with stainless steel, have obtained the approval of the competent superintendence offices.
Over the years, the collaboration between Kerakoll and the world of academia has aided the rapid transfer of scientific research to professional practice, contributing to the development of reliable, durable technical solutions. The systems proposed respond to multiple structural requirements, such as combating out-of-plane tipping, increasing the bending and cutting resistance of vertical load-bearing walls, confining columns and pillars, reinforcing arches, vaults and architraves, repairing elements that protrude upwards or outwards (such as chimney flues and ledges), restoring statues, stone frames, capitals and other decorative elements.