Graça Vasconcelos et al, Integrated experimental analysis for the characterization of historical mortars, Revista Mecânica Experimental, Nº 37, APAET (2026), pp. 71 -81.

Integrated experimental analysis for the characterization of historical mortars

Análise experimental integrada para a caracterização de argamassas históricas

Graça Vasconcelos[1] | **Rafael Ramirez**[1] | **Paulo B. Lourenço**[1]

[1] ISISE– Instituto para a Sustentabilidade e Inovação em Engenharia de Estruturas, Departamento de Engenharia Civil, Universidade do Minho, Portugal

https://doi.org/10.82452/me20263707

abstract

Accurate characterization of historic mortars is essential for the conservation and restoration of masonry structures, ensuring compatibility with original materials and preventing long-term damage caused by inappropriate repair mortars. Historic mortars are heterogeneous materials whose properties reflect original construction practices and subsequent environmental exposure. This study presents an integrated characterization of a late 19th-century mortar from the Land Management Building of the Lviv National University of Environmental Management (Dubliany), Ukraine. Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) were used to identify binder and aggregate phases. Density, open porosity, and compressive strength were determined using hydrostatic and double punch tests on small specimens. The results highlight the effectiveness of a multi-analytical approach for reliable identification of historic mortar properties.

Keywords: Conservation and restoration, historic mortars, binder and aggregates, experimental characterization

resumo

A caracterização de argamassas históricas é essencial para a conservação e o restauro de estruturas de alvenaria, garantindo a compatibilidade com os materiais originais e prevenindo danos a longo prazo causados por argamassas de reparação inadequadas. As argamassas históricas são materiais heterogéneos, cujas propriedades refletem as práticas construtivas originais e a exposição ambiental ao longo do tempo. Este estudo apresenta a caracterização integrada de uma argamassa do final do século XIX, proveniente do edifício da Universidade Nacional de Gestão Ambiental de Lviv, em Dubliany, Ucrânia. Técnicas de microscopia eletrónica de varrimento com espectroscopia de dispersão de energia (SEM-EDS), difração de raios X (XRD), espectroscopia de infravermelhos por transformada de Fourier (FTIR) e análise termogravimétrica (TGA) foram utilizadas para identificar as fases do ligante e dos agregados. A densidade, a porosidade aberta e a resistência à compressão foram determinadas através de ensaios hidrostáticos e de ensaios de compressão uniaxial em provetes de pequena dimensão. Os resultados evidenciam a eficácia de uma abordagem experimental integrada para a identificação fiável das propriedades de argamassas históricas.

.Palavras-chave: Conservação e restauro, argamassas históricas, ligantes e agregados, caracterização experimental

1- INTRODUCTION

In restoration and conservation works in historical masonry structures/buildings, the understanding the properties of the raw materials used in mortars and plasters is crucial for selecting appropriate materials for restoration. This is of particular importance when conservation principles focused on the maintenance of aesthetics, historical significance and compatibility with original materials is mandatory [1,2]. Historic structures frequently undergo multiple repair episodes. Inappropriate restoration mortars (e.g., Portland cement–rich mixes from 20th-century interventions) can alter the mortar matrix and create compatibility issues, such as differential strength and stiffness, moisture and salt trapping, or accelerated decay of adjacent historic materials (bricks/stones).

Therefore, the accurate identification and characterization of historic mortars is a foundational step in the conservation and restoration of built heritage. Historic mortars are complex, heterogeneous materials whose composition and long-term alterations reflect both the original construction technology and centuries of environmental and mechanical interactions [3-5]. Mortars may contain a mix of binders (e.g., lime, gypsum, mud), aggregates of varying mineralogy and granulometry, and additives (e.g., pozzolans, organic fibers).

Despite the availability of modern analytical tools, significant challenges persist in reliably identifying the raw materials, namely binders and aggregates, the binder to aggregate ratio, and, in particular, physical and mechanical properties due to the difficulty to obtain reliable and appropriate dimension samples. In this scope, archaeometry analyses based on optical and high-resolution microscopy (SEM-EDS), X-ray diffraction (XRD) and FTIR play a critical role in determining the nature of the binder and aggregates [6-7].

This work focuses on the integration of different characterization techniques aiming at identifying the binder and aggregates, as well as physical and mechanical properties of a historical mortar belonging to the Land Management Building of the Lviv National Environmental University (LNAU) in Dubliany, dating to the late 19th century. Advanced experimental characterization techniques such scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray diffractometry (XRD) and FTIR complemented with thermogravimetric analysis (TGA) were used to identify the binders and type of aggregate. Porosity tests and double punch tests were carried out on small mortar specimen to obtain density, open porosity and compression strength respectively.

2- MATERIAL AND METHODS

2.1. Brief description of mortar

The mortar samples used for experimental characterization were collected from bed joints of the original brick masonry of the Land Management Building of LNAU, located in Dubliany (Lviv, Ukraine). The building dates from the late nineteenth century (1888) and represents an institutional masonry construction of that period. Sampling was carried out at the top of a second-floor masonry wall. This area became accessible after the removal of the roof, as well as the attic walls and slabs, which had suffered extensive damage due to a drone attack and were deemed highly unstable.

The extracted specimens presented irregular shape, see Fig. 1. In few cases, localized cracking was observed, likely associated with the removal process. All samples present a whitish color. Visual inspection indicates a relatively uniform distribution of aggregates within the binder matrix. The mortar incorporates sand with predominantly fine to medium particle sizes, which appear well embedded in the matrix. Due to the limited amount of available material, sieve analysis for grain size distribution was not performed.

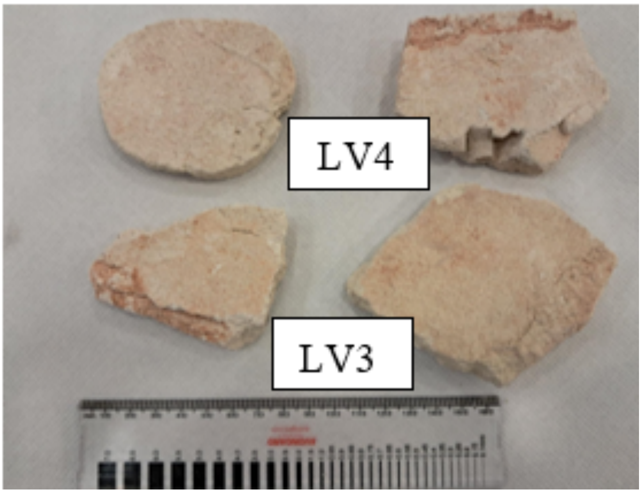


Fig. 1 | Examples of mortar samples removed from the joints of brick masonry - Lviv National Environmental University (Lviv, Ukraine).

2.2. Experimental methods

The experimental characterization of mortar aimed at obtaining the main compounds, namely the mineral phases that can be associated with binder and aggregates composing the mortar. For this purpose, it was decided to carry out complementary tests, able to identify the main inorganic compounds and to assess the presence of contamination (such as organic compounds or gypsum) or salts. Four complementary tests were adopted, namely (a) X-ray diffraction (XRD); (b) Scanning Electron microscopy and X-ray microanalysis with Energy Dispersive Spectroscopy (SEM-EDS); (c) thermal analysis (TGA); (d) Fourier Transform Infrared Spectroscopy (FTIR) analysis. Mortar samples to be used in the testing campaign to identify the raw materials were cleaned with a small saw to remove the brick particles attached. After this, part of the sample was disaggregated to be reduced to a fine powder (Fig. 2a).

After disaggregation, the mortar was ground with a very hard stone until reaching a very small particle size, see Fig. 2a. Only the very small particles passing in the sieve of 63 μm were used for TGA, XRD and FTIR analysis (Fig.2 b,c).

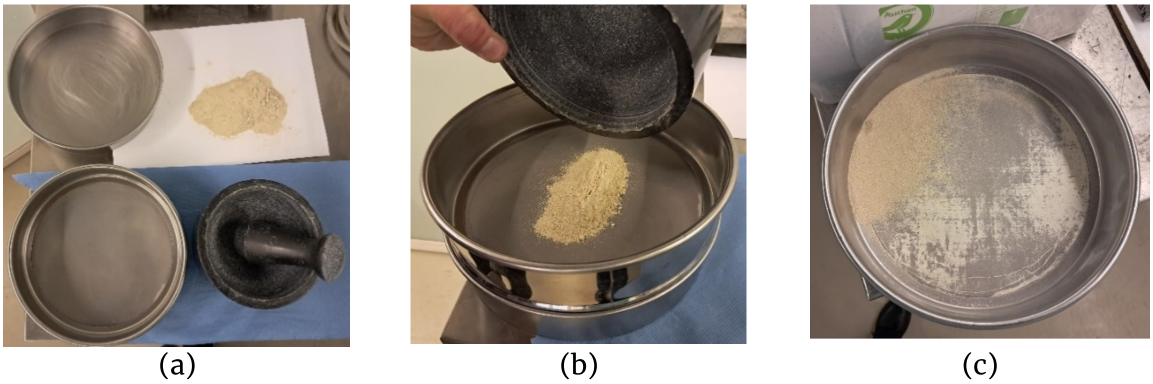

(a) (b) (c)

Fig. 2 | Preparation of samples for TGA, XRD and FTIR analysis; (a) disaggregated mortar, grinding device and sieve; (b)(c) ground material before and after sieving.

2.2.1 Thermal analysis

Thermal analysis is an experimental technique used to investigate the physical and chemical behavior of materials as a function of temperature. Thermogravimetric analysis (TGA) measures the variation in mass of a sample during controlled heating, which results from different thermal processes such as dehydration, dehydroxylation, decarbonation, oxidation, decomposition, phase transformations, or melting. These thermal events occur within specific temperature ranges that are characteristic of the mineralogical phases and hydrated compounds present in the material. Differential thermogravimetry (DTG) corresponds to the first derivative of the thermogravimetric curve and provides information on the rate of mass loss, allowing a more precise identification of the temperature ranges associated with individual thermal reactions.

According to [8], in aerial lime binders, mass loss related to the release of hygroscopic water occurs below 100 °C, while the loss of interstitial (physically bound) water generally takes place up to approximately 150 °C. The release of chemically bound water from hydrated phases typically occurs between 120 °C and 200 °C. Mass loss observed in the range between 600–850 °C is mainly attributed to the release of carbon dioxide during the decomposition of calcium carbonate (calcite), corresponding to the decarbonation reaction. As noted in [9], the decomposition of calcium carbonate may occur at lower temperatures (approximately 500–600 °C) when salts are present in the mortar, as they can catalyze or modify the reaction. The decomposition of calcium hydroxide (portlandite) generally occurs between 350 °C and 450°C.

Thermogravimetric analysis of the mortars was performed using an SDT Q600 instrument under a nitrogen atmosphere, with a heating rate of 10 °C/min. Two samples from the Lviv mortar were analyzed, corresponding to the same samples used in the FTIR analysis.

2.2.2 XRD analysis

With the aim of identifying the mineralogical phases present in the mortars under analysis, X-ray diffraction (XRD) was performed on one sample from the Lviv mortar. The XRD measurements were conducted in θ–2θ geometry at room temperature using a Bruker AXS D8 Discover diffractometer (Karlsruhe, Germany), equipped with a silicon strip–based LynxEye detector (Bruker). Diffractograms were collected in the 2θ range from 5° to 80°, with a step size of 0.02° and a counting time of 1 s per step. Phase identification was carried out using Bruker AXS DIFFRAC.EVA software (version 4.2.2) in conjunction with the ICDD (International Centre for Diffraction Data) database. In addition, quantitative phase analysis was performed to estimate the relative abundance of the identified phases. For this purpose, the TOPAS software was employed, fitting the experimental diffraction patterns through structural refinement based on the Rietveld method.

2.2.3 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is a complementary technique to XRD for the characterization of historic mortars and binders, as it allows the identification of inorganic phases and organic functional groups through the vibrational response of molecular bonds under infrared radiation. Based on the literature, FTIR spectra enable the identification of key mortar constituents, including calcite, portlandite, gypsum, quartz, calcium silicate hydrates (C–S–H), and structural or free water, each characterized by specific absorption bands within the infrared spectrum [10, 11]. FTIR measurements were carried out using a Shimadzu Fourier transform infrared spectrophotometer (IRAffinity-1S). Spectra were recorded over the range 400–4000 cm^{-1}, with a resolution of 4 cm^{-1} and averaging approximately 45 scans per sample. One sample of mortar was analyzed.

2.2.4 SEM Analysis

Morphological analyses were carried out in an Ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company at an acceleration voltage between 10 and 15 kV. Chemical analyses were performed by X-ray microanalysis with Energy Dispersive Spectroscopy (EDS) technique, using an EDAX Si(Li) detector, integrated in the SEM, using an acceleration voltage of 25 kV. With this analysis, it is intended to obtain insights into the binder composition, hydration products, and carbonation effects. All samples were coated with gold. In SEM-EDS analysis, one sample of Lviv mortar was considered (LV).

2.3 Physical characterization

The density and open porosity of the mortars were determined using small irregular samples, some of which were extracted from specimens previously tested under uniaxial compression (Fig. 3). Both density and open porosity were measured using the hydrostatic method in accordance with EN 1936 [12].

Prior to testing, the samples were dried in an oven at 60 °C until constant mass was achieved. The dry mass (Md) was considered constant when the difference between two consecutive measurements taken 24 hours apart was less than 0.1% of the average of the two measurements. The samples were then saturated by water immersion following a multi-step procedure: 4 hours under dry vacuum to remove air from the open pores, 4 hours of saturation under vacuum, and subsequent immersion at atmospheric pressure for an additional 24 hours. After saturation, the saturated mass (Msat) and the submerged mass (Msub) were measured.

Fig. 3 | Samples for density and open porosity tests.

2.4 Mechanical characterization

Given the irregular shape, small size, and non-standard geometry of the mortar samples extracted from brick masonry joints, double punch tests (DPT) were adopted to determine the compressive strength of the mortars. This method represents a suitable alternative to conventional compression tests when only very small specimens are available. The testing procedure generally followed the DIN 18555-9 standard [13].

According to the standard, the height of the mortar specimens corresponds to the bed joint thickness, while the in-plane dimensions should be approximately 50 mm. In the present study, due to the limited size and weak nature of the specimens, the samples were tested in their original irregular shape and were not cut to the dimensions prescribed by the standard. The mortar specimens were loaded using steel punches with a diameter of 20 mm (Fig. 4a). To ensure proper load transfer and alignment, gypsum capping was applied to the upper and lower loading areas of the specimens, providing leveled surfaces and promoting uniform compressive loading.

In total, four specimens of Lviv mortar were tested. As the specimen thickness was not uniform, the average thickness was determined as the mean value of five measurements taken for each specimen. The mortar compressive strength obtained from the DPT was calculated as the ratio between the maximum applied force and the cross-sectional area of the steel punch. The tests were performed using an electromechanical testing machine (MTS, Model E45) under displacement control, with a loading rate of 5 μm/s. The machine had a maximum load capacity of 100 kN.


(a) (b) (c)

Fig. 4 | Double Punch Tests; (a) setup apparatus; (b) (c) failure of the specimen

3- RESULTS AND DISCUSSION

3.1 Identification of raw materials

The X-ray diffractogram of the mortar sample is shown in Fig. 5. The diffraction pattern exhibits strong correspondence with reference patterns of calcite ($CaCO_3$) and quartz (SiO_2). Accordingly, the identified crystalline phases are rhombohedral calcite and hexagonal quartz. In addition, the presence of a rhombohedral dolomite phase was detected with a lower degree of confidence. Further confirmation of dolomite would require complementary analyses, such as elemental chemical characterization by SEM–EDS. Quantitative phase analysis performed through Rietveld refinement using TOPAS software indicated phase contents of 87.90% calcite, 10.92% quartz, and 1.18% dolomite.

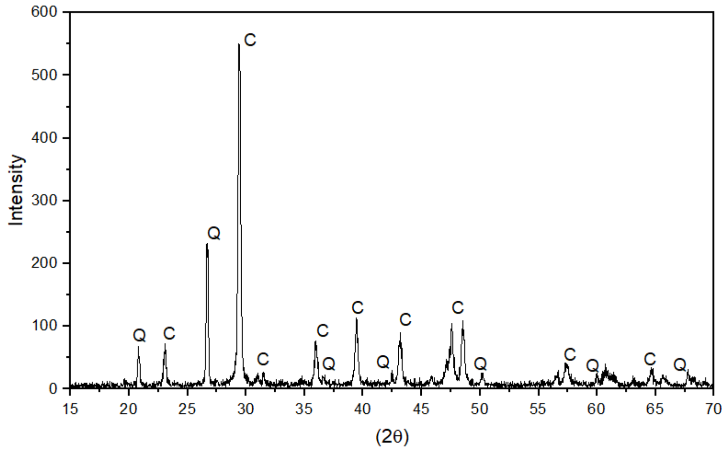


Fig. 5 | XRD diffractogram from Lviv mortar (C - Calcite; Q - Quartz).

Fig. 6 shows the FTIR spectrum obtained for the Lviv mortar sample. The spectrum indicates a dominant presence of calcite ($CaCO_3$), evidenced by the strong absorption bands at 1392 cm^{-1} (asymmetric stretching of CO_3^{2-}), 871.8 cm^{-1} (out-of-plane bending of CO_3^{2-}), and 711.7 cm^{-1} (in-plane bending of CO_3^{2-}).

Absorption bands at 451.3 cm^{-1} and 418.6 cm^{-1}, attributed to Si–O bending vibrations, indicate the presence of quartz associated with the silica sand aggregate. In addition, the band at 1011 cm^{-1} corresponds to Si–O–Si asymmetric stretching vibrations, further confir-

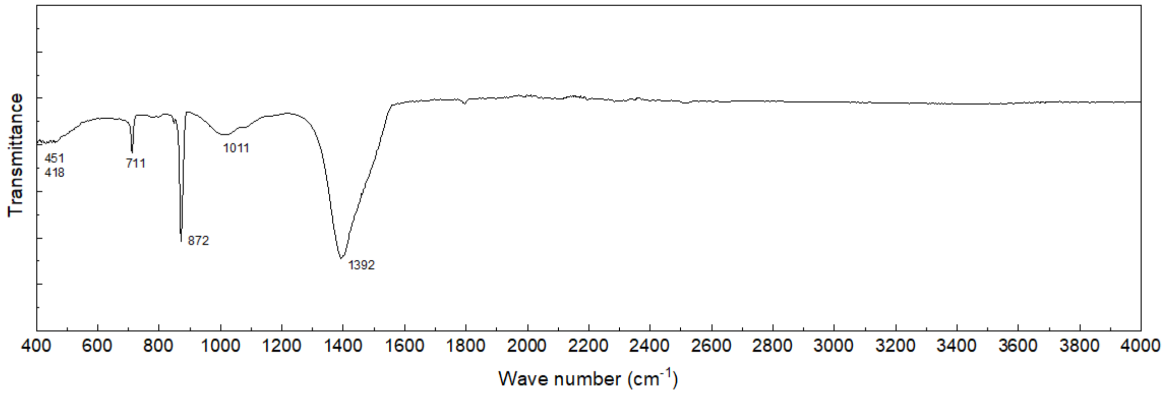


Fig. 6 | FTIR spectra

ming the presence of quartz in the mortar. Characteristic bands of portlandite (calcium hydroxide, $Ca(OH)_2$), typically observed at approximately 3641 cm^{-1} (O–H stretching) and 1641 cm^{-1} (H–O–H bending), were not detected. This absence indicates that the mortar binder is fully carbonated.

The thermogravimetric (TG) curves for two Lviv mortar powder samples are shown in Fig. 7. Both samples exhibit a small endothermic mass loss from ambient temperature up to approximately 52 °C, corresponding to the release of free or hygroscopic water, with a total weight loss of about 0.7% of the initial mass. A second, more pronounced mass loss occurs between 600 °C and 800 °C, corresponding to the decomposition of calcium carbonate. The temperature ranges for these reactions were more precisely identified using the differential thermogravimetric (DTG) curves, which indicate the temperature of maximum weight change at approximately 770 °C for the calcium carbonate decomposition.

No significant weight loss is observed in the temperature range associated with the dehydroxylation of calcium hydroxide, suggesting that the binder in the mortar is aerial lime that has undergone complete carbonation [9]. Furthermore, the TG analysis shows no evidence of other compounds, such as gypsum or silicates, consistent with the XRD results that identified only calcite and quartz. In this context, calcite is attributed to the carbonation of the lime binder, while quartz corresponds to the silica sand aggregates.

Based on the mass loss associated with the 600–800 °C endothermic peak and considering the molecular masses of CO_2 (44 g/mol) and $CaCO_3$ (100 g/mol), the calcium carbonate content in the mortar samples was estimated. The analysis indicates that the mortar contains, on average, 71.0% calcium carbonate, confirming a substantial presence of this phase in the material.

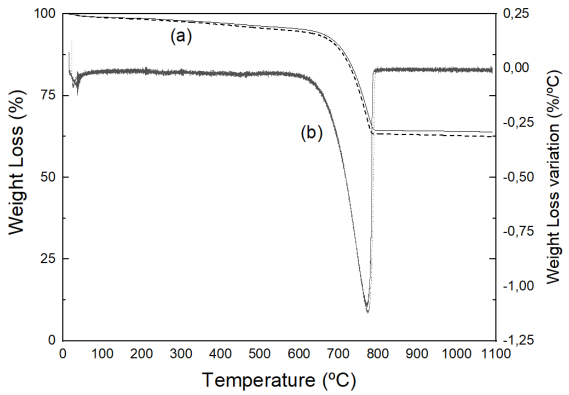
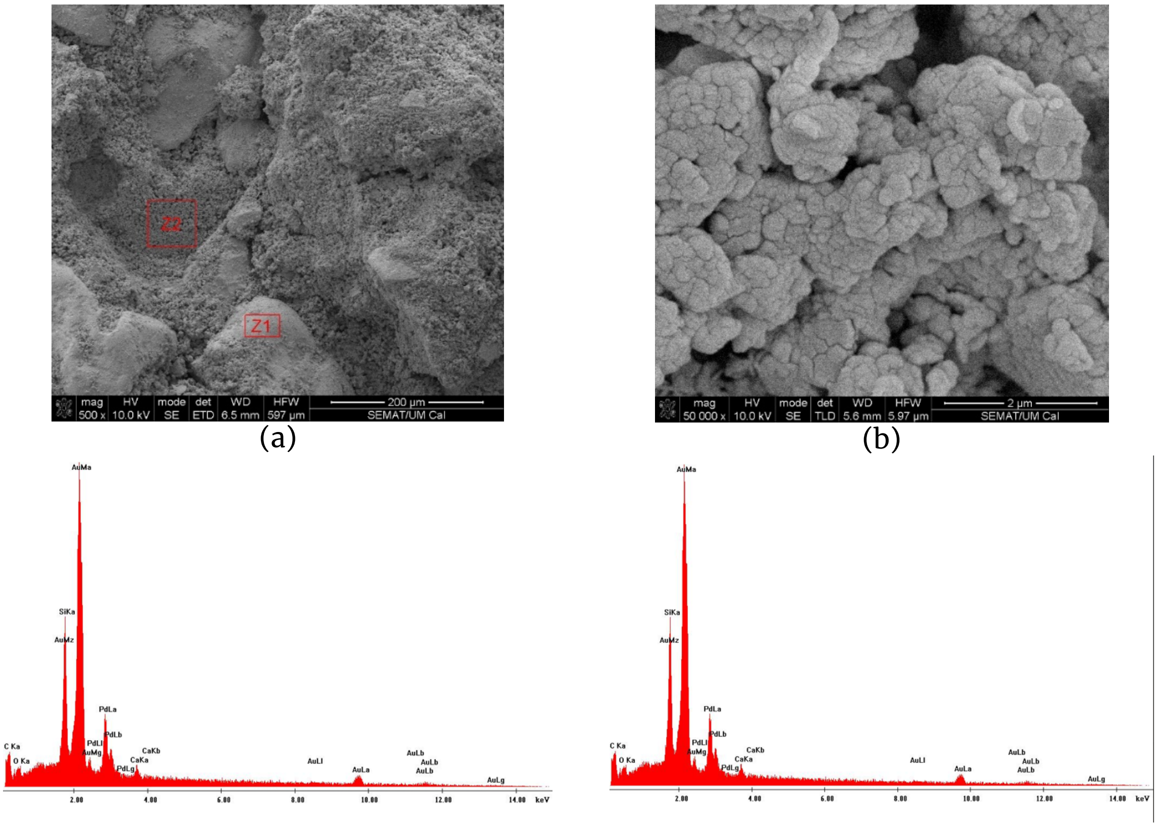


Fig. 7 | TGA analysis of two samples from LVIV mortar (a) TGA curve (b) DTG curve

The SEM image of the mortar sample at 500× magnification shows a well-bonded binder matrix surrounding the aggregates (Fig. 8a). EDS spectra were collected from two distinct regions: the matrix (Zone Z2) and the aggregate (Zone Z1). Zone Z2 exhibits a high calcium content with comparatively lower carbon and oxygen levels, consistent with the presence of carbonates (Fig. 8c). Zone Z1 is enriched in silicon and oxygen, indicating a silica-rich aggregate, likely silica sand dominated by quartz, in agreement with the XRD analysis (Fig. 8d).

At higher magnification (50,000×), Zone Z2 reveals agglomerates of rounded, cauliflower-like particles (Fig. 8b), interpreted as recrystallized calcite. This observation is consistent with the XRD results, which identified calcite as the sole mineralogical phase in the binder.



(a) (b)

(c) (d)

Fig. 8 | Images of SEM-EDS analysis of Lviv mortar: (a) image at 200 μm amplification; (b) image at 2 μm amplification; (c) EDS spectra – Zone Z1 1; (d) EDS spectra – Zone Z2

3.2 Physical and mechanical properties

The density and open porosity values of the mortar samples are summarized in Table 1. The average density of the Lviv mortar samples is 1645 kg/m³ (Cv = 1.4%). The values of open porosity found for Lviv mortar are in the range attributed to air lime mortars [14].

The maximum load recorded for all tested samples and the corresponding compressive strength determined from the Double Punch Test (DPT) are reported in Table 2. The average compressive strength of the Lviv mortar samples is approximately 1.96 MPa, with a standard deviation of 0.30 MPa and a coefficient of variation of 15.3%.

The typical failure mode associated with the DPT was observed: cracks propagated radially from the loaded region of the specimens (Fig. 4b). Due to confinement effects, the material surrounding the steel punches tended to form a double-cone shape upon failure (Fig. 4c).

Table 1 | Density and open porosity of mortars

Specimen	Density (Kg/m³)	Porosity (%)
LV 1	1660.8	37.3
LV 2	1663.2	37.1
LV 3	1611.7	38.9
LV 4	1646.1	37.6

Table 2. Double Punch compression strength of mortar

Specimen	Average thickness (mm)	Load max (N)	F_{cDPT} (MPa)
LV1	14.2	648.40	2.06
LV2	17.0	488.33	1.55
LV3	14.3	712.84	2.26
LV4	19.6	618.47	1.97

5- CONCLUSIONS

The characterization of the Lviv mortar, sampled from the Agrarian University of Dubliany, indicates that it is a fully carbonated aerial lime mortar composed primarily of lime binder and silica sand aggregates. Key findings are as follows:

- Thermal analysis (TGA/DTG) shows that, aside from the loss of free water at low temperatures, the only significant chemical decomposition occurs between 600 °C and 800 °C, corresponding to calcium carbonate decomposition. No dehydroxylation of portlandite ($Ca(OH)_2$) was observed, confirming complete carbonation of the binder.
- X-ray diffraction (XRD) identifies predominantly calcite and quartz, consistent with an aerial lime binder and silica sand aggregates.
- FTIR spectroscopy reveals dominant calcite peaks and no evidence of portlandite, further supporting full carbonation. Quartz-related vibration bands confirm the presence of silica sand aggregates.
- SEM-EDS analysis shows a well-carbonated microstructure with characteristic cauliflower-like morphology of binder particles. EDS spectra indicate silica aggregates embedded in a calcium carbonate–rich matrix.
- Density and open porosity measurements are consistent with values reported for aerial lime mortars, with high porosity typical of such materials.
- Mechanical testing (Double Punch Test) on four irregular specimens yields an average compressive strength of approximately 2.0 MPa, in line with fully carbonated lime mortars.

Overall, these results confirm that the Lviv mortar is a well-carbonated aerial lime mortar with silica sand aggregates, exhibiting physical and mechanical properties typical of historic lime-based mortars.

ACKNOWLEDGEMENTS

This work was supported by FCT/MCTES under the R&D Unit Institute for Sustainability and Innovation in Structural Engineering (ISISE), under the references UID/4029/2025 (https://doi.org/10.54499/UID/04029/2025) and UID/PRR/04029/2025 (https://doi.org/10.54499/UID/PRR/04029/2025), and under the Associate Laboratory Advanced Production and Intelligent Systems ARISE under reference LA/P/0112/2020.

REFERENCES

[1] ICOMOS, Icomos Charter- Principles for the Analysis, Conservation and Structural Restoration of Architectural Heritage, Archit. Herit., 2003.

[2] ISCARSAH, Recommendations for the analysis, conservation and structural restoration of architectural heritage, Int. Counc. Monum. Sites, 2003.

[3] Magalhães, A., Veiga, R. Physical and mechanical characterization of historic mortars. Application to the evaluation of the state of conservation, Materiales de Construcción, 59, 295, 61-77, 2009.

[4] Schueremans, L., Cizera, O., Janssensa, E., Serréa, G., Van Balen, K. Characterization of repair mortars for the assessment of their compatibility in restoration projects: Research and practice, Construction and Building Materials, 25, 4338-4350, 2011.

[5] Loke, M.E., Kumar, P., Cultrone, G. Challenges in characterization and development of suitable historic repair mortars, International journal of Conservation Science, 14(3), 783-802, 2023.

[6] Groot, C., Ashall, G., Hughes, J., Bartos, P. Characterization of old mortars with respect to their repair: a state of the art, RILEM Rep., 28 (2007).

[7] Borsoia, G., Santos Silva, A., Menezes, P., Candeias, A., Mirão, J. Analytical characterization of ancient mortars from the archaeological roman site of Pisões (Beja, Portugal), Construction and Building Materials, 204, 567-608, 2016.

[8] A. Bakolas et al., “Thermoanalytical research on traditional mortars in venice,” Thermochim. Acta, vol. 269–270, no. C, pp. 817–828, 1995. doi: 10.1016/0040-6031(95)02574-X.

[9] Ö. Cizer, C. Rodriguez-Navarro, E. Ruiz-Agudo, J. Elsen, D. Van Gemert, and K. Van Balen, “Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime,” J. Mater. Sci., vol. 47, no. 16, pp. 6151–6165, 2012.

[10] A. Diekamp, R. Stalder, J. Konzett, and P. W. Mirwald, “Lime mortar with natural hydraulic components: characterisation of reactionrims with FTIR imaging in ATR-Mode.,” in Valek J et al (eds) Historic mortars: characterisation, assessment and repair, 2012, pp. 105–113.

[11] M. M. Jordán, J. Jordá, F. Pardo, and M. A. Montero, “Mineralogical analysis of historical mortars by FTIR,” Materials (Basel)., vol. 12, no. 1, pp. 10–14, 2018, doi: 10.3390/ma12010055.

[12] EN 1936. Natural stone test methods - Determination of real density and apparent density, and of total and open porosity, 2006.

[13] DIN. 18555-9:2019-04, Prüfung von Mörteln mit Mineralischen Bindemitteln—Teil 9: Festmörtel; Bestimmung der Fugendruckfestigkeit; DIN: Berlin, Germany, 2019.

[14] Kumar, D.N., Kumar , P.R. Investigations on alternate lime-pozzolana based mortars for repair of heritage structures, Construction and Building Materials 341, 127776, 2022.