International Symposium on the Conservation of Monuments in the Mediterranean Basin

(2024)

Proceedings of the 11th MONUBASIN (2024)

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doi: [10.12681/monubasin.8174](https://doi.org/10.12681/monubasin.8174)

Characterization of mortars from the Vartalis Watermill in Cyprus

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Abstract. Traditional watermills for grain production are found in many places across the world. However, despite being an integral part of rural agriculture throughout history, these structures have received relatively little attention compared to other monuments and traditional buildings. Hence, studies of their building materials, including mortars, remain scarce. This paper focuses on the assessment of four mortar samples received from the Vartalis watermill in Cyprus. The study is part of a wider project focusing on the building materials (especially mortars) of a number of watermills around Nicosia and Cyprus. Two of the four mortar samples investigated were extracted from the aqueduct leading to the water tower, while the remaining two were obtained from the water tower of the watermill. In both cases, the mortars were in direct contact with water whilst the water tower was operative. Therefore, the assessment involved an insight into their consistency and hydraulic properties. Macroscopic observations and laboratory analytical experimental techniques, which included powder X-Ray Diffraction (XRD) analysis on the binder/aggregate fractions separately and Thermogravimetric and Differential Thermal Analysis (TG-DTA) on the bulk samples, were employed for the detailed study and characterization of the mortars. The results showed that all four mortar samples were consistent, with densely packed river sand as aggregate material and the occasional presence of lime lumps and coal. They also revealed the presence of calcite and crushed ceramic in the binder fraction, as well as quartz and plagioclase (albite) in the aggregate fraction. Notably, the CO_2/H_2O ratio of the samples ranged between 1.2 and 3, suggesting that these may be classified as strongly hydraulic lime mortars.

Keywords: Lime mortars, Watermills, XRD, TG-DTA.

1 Introduction

Hydraulic mortars consisting of aerated lime and fired clay brick powder were used in the past in structures where protection from water and humidity was required [1]. In fact, the utilization of crushed brick-lime mortars in Cyprus traces back to the Late Bronze Age. The use of crushed brick, an artificial pozzolanic additive, in prehistoric mortar production technology in Cyprus has been attributed to the absence of natural pozzolans on the island [2, 3]. Crushed brick-lime mortars have been identified in various water-related structures across Cyprus to date; these include water channels, baths, workshops, and watermills [4, 5].

Cypriot watermills have been an integral part of the island's traditional rural life, economy, and cultural heritage. There are over 650 watermills scattered across the island; most of these have been in use until the middle of the 20th century [6]. However, during the British Colonial period, technological innovations led to the industrialization of the local society. This inevitably led to the decline of Cypriot watermills. Notably, while in 1919, 400 watermills operated simultaneously alongside windmills, animal-driven flour mills, and steam mills on the island, during the 1930s, traditional watermills decreased in number while steam mills gradually increased. Eventually, in the 1950s, traditional watermills were replaced with engine-driven mills [7]. Nowadays, most of the watermills in Cyprus are abandoned.

A number of studies on Cypriot watermills have been attempted lately [8]. Nevertheless, studies of their building materials, including mortars, still remain scarce [5]. This paper focuses on the assessment of four representative mortar samples received from the Vartalis watermill located in the village of Agios Ioannis in Nicosia district (Cyprus). The aim of the investigation is the characterization of the aforementioned samples and the potential identification of any natural or artificial pozzolanic additives.

2 The watermill of Vartalis

The watermill of Vartalis is situated within the administrative boundaries of Klirou, Malounta and Agios Ioannis villages, on the west bank of the Akaki River, in Nicosia district (Cyprus – Sheet/Plan: 29/ 47E2 - Parcel No.: 282) (Fig. 1) [9]. It was constructed either in 1841 or 1856 and remained operative until World War II. In 1979, it was declared an Ancient Monument.

The mill (Fig. 2) is well preserved and retains the aqueduct, the water tower with its pit, the main room with the grinding mechanism, the underground room which housed the waterwheel, and traces of an auxiliary room. It is built of local limestones and river pebbles, while the interior surfaces of the aqueduct and the water tower are plastered.

Fig. 1. Map of Cyprus showing the location of the Vartalis watermill.

Fig. 2. Aerial view of the Vartalis watermill, showing the sampling locations.

3 Materials and Methodology

Four mortar samples were extracted from the preserved remains of the Vartalis watermill (see Fig. 2) using a hammer and chisel. Two of these samples are classified as jointing mortars and were extracted from the aqueduct (AGIM 1-3) and the water tower (AGIM 1-6), while the remaining two are classified as plasters and were collected from the interior of the walls of the aqueduct (AGIM 1-4) and the water tower (AGIM 1-1).

The samples were first observed macroscopically, both on-site and in the lab, using a stereomicroscope. Their binder was then separated from the aggregates, following cycles of sonication and sieving through a 63 μm sieve. This helped determine the binder/aggregate (B/A) ratio of each sample, whilst it also provided individual samples for some of the analyses that followed.

Simultaneous Differential Thermal Analysis (DTA) and Thermogravimetry (TG) on each sample were then carried out with a Shimadzu DTG – 60H analyzer, using specimens of mass 20-70 mg. The bulk samples were placed in alumina crucibles and the analyses were conducted under atmospheric air, from room temperature to 1200°C, at a heating rate of 5°C/min.

In addition, powder X-Ray Diffraction (XRD) analysis on the binder and aggregate fraction of each sample was performed separately, using a Bruker D8 Advance system with Cu K_α radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA. The analyses were carried out with continual rotation of the sample and a scanning speed of 2°/min, within the 2-70° 2θ angle range. The International Centre for Diffraction Data (ICDD) PDF 4 database was used for the qualitative identification of the constituent mineral phases.

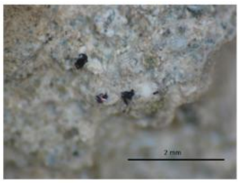
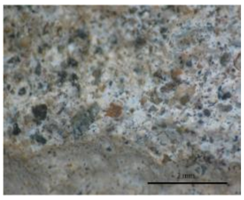
4 Results and Discussion

4.1 Macroscopic and microscopic observations

Preliminary macroscopic observations of the bulk specimens showed that all four samples were made of the same type of raw materials (see Table 1). Most of the samples appeared to be light grey or grey in color. The mortars extracted from the water tower were harder and more compact compared to those extracted from the aqueduct. The two mortars extracted from the interior walls of the aqueduct and the water tower were characterized by smooth external surfaces. None of the samples showed evidence of the presence of layers; all samples could be described as homogenous.

Further observations under the stereomicroscope revealed that the mortar samples were consistent with densely packed river sand as aggregate material; the latter ranged from ca. 0.2 to 2 mm in grain size and comprised various colors and shapes (see Table 1). In all samples, mainly subangular to rounded aggregate particles with grey and dark brown colors were identified, while the color of the binder was mostly whitish, suggesting a calcitic origin. Moreover, within the binder matrix of some samples, lime lumps measuring up to 2 mm were observed (see Table 1), the presence of which is common in historic lime mortars, indicating an incomplete calcination process [3]. It is noteworthy that lime lumps were identified only in the samples extracted from the water tower of the mill (AGIM 1-1 and AGIM 1-6). Sample AGIM 1-1 further showed evidence of the presence of some subangular and extremely fine reddish clay inclusions with grains < 1 mm. In sample AGIM 1-3, traces of coal were observed.

Table 1. Macroscopic and microscopic characteristics of the mortar samples collected from the Vartalis watermill.

Sample	Sampling location	Photo (in hand)	Photo (stereomicroscope)
AGIM 1-1	Water tower – Plaster		
AGIM 1-3	Aqueduct – Plaster		
AGIM 1-4	Aqueduct – Plaster		

AGIM 1-6	Water tower - Jointing mortar		

4.2 Binder/aggregate ratios

The binder/aggregate ratios of the four mortar samples hereby studied ranged from 1:2 to 1:3. The B/A ratio of 1:3 is the most common one cited in the literature [10, 11] and aligns with the ancient technological "standards" concerning crushed brick-lime mortars, as outlined by Vitruvius [11].

4.3 Thermal analyses

The thermal analysis results confirmed that the mortar samples under study may be classified as strongly hydraulic. The graphs obtained during these analyses (Fig. 3) correspond to similar graphs found in the literature for hydraulic lime mortars [12].

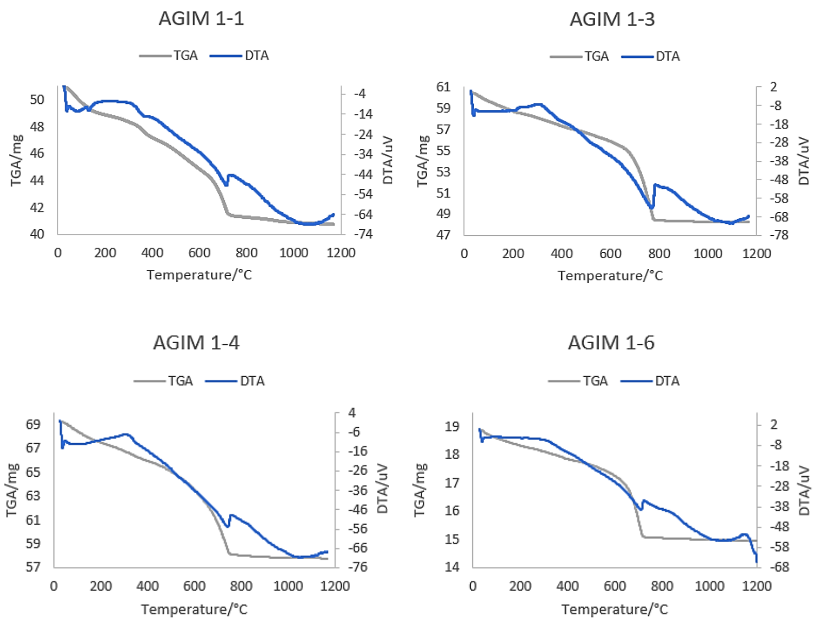


Fig. 3. DTA/TGA curves of the mortar samples under study.

In the graphs above, the first endothermic peak shown in the DTA curves, occurring between 40–60°C, is attributed to the loss of absorbed water from the mortars [13]. The second peak, between 120-200°C, which is more prominent in samples AGIM 1-1 and AGIM 1-3, corresponds to the loss of chemically bound water from hydrated salts, such as gypsum ($CaSO_4 \cdot 2H_2O$) [14]. The presence of gypsum may indicate mortar deterioration arising from reaction with atmospheric pollutants, or it might have been intentionally added to the mortar mixture [15, 16]. The limited amount observed in the analyzed samples suggests that gypsum is rather incidental, possibly due to environmental pollution. The exothermic peak at ca. 300°C suggests the loss of organic material [17].

Weight loss between 200 and 600°C is attributed to the release of chemically bound water from hydraulic compounds, such as calcium silicate hydrates and calcium aluminate hydrates [1, 12, 18]. These hydraulic products usually form following a reaction between lime and ceramic fragments [19]. Between 350 and 400°C, a reaction was detected in sample AGIM 1-1; similarly, two imperceptible reactions between 450 and 550°C were observed in sample AGIM 1-3. Both aforementioned reactions indicate the presence of portlandite [20, 21, 22].

The loss in weight occurring > 600°C is associated with the release of CO_2 due to the decomposition of carbonate minerals (calcite and/or dolomite) [15, 18, 23]. Usually, the thermal decomposition of carbonate minerals begins at temperatures > 600 to 650°C and continues until 750 to 850°C [15]. In the samples analyzed in this study, the carbonate decomposition reaction occurred between 700-800°C. Endothermic reactions within these temperatures (see DTA curves in Fig. 3) confirm the calcitic origin of the binder of the mortars. The mass loss at ca. 750°C may also indicate the loss of CO_2 due to the use of re-carbonated lime within certain cementitious materials, in which the original limestone contained specific clay minerals [18]. Calcite decomposition at temperatures < 850°C further suggests the use of impurities, such as magnesian lime or clays [23].

Through thermal analysis, the degree of hydraulicity of the mortars can be determined. This is defined as the ratio between the amount of CO_2 lost and the amount of H_2O linked to hydraulic compounds. A higher CO_2/H_2O ratio corresponds to less hydraulic mortars [24, 25, 26]. The calculated values of the ratio CO_2/H_2O of the mortars hereby examined are reported in Table 2. These ranged between 1.2 and 3, suggesting that the mortars under study may be classified as strongly hydraulic [15, 23].

Table 2. Water and CO_2 mass loss calculated from thermal analyses and hydraulicity ratios.

Sample	H_2O Loss (%)			CO_2 Loss (%)	CO_2/H_2O
	<120°C	120°C-200°C	200°C-600°C	>600°C	
AGIM 1-1	2.7	1.3	6.5	8.0	1.2
AGIM 1-3	1.6	1.2	4.5	11.6	2.6
AGIM 1-4	1.5	0.5	4.1	10.6	2.6
AGIM 1-6	1.9	1.1	4.5	13.4	3.0

4.4 X-Ray Diffraction

The mineralogical composition of the binder and aggregate fractions of the four mortars hereby studied is shown in Fig. 4.

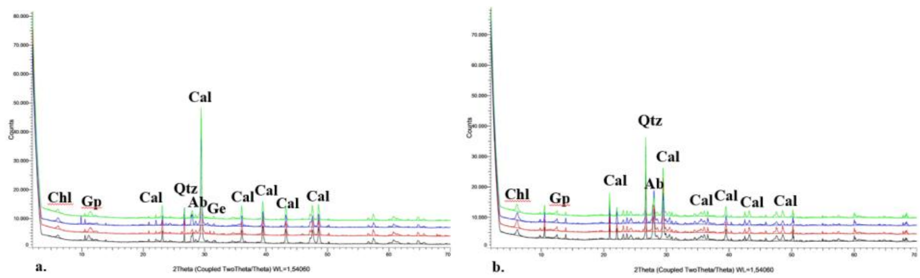


Fig. 4. Powder XRD patterns of the binders (a) and aggregates (b) of the mortars under study (some minor peaks have not been identified for clarity).
(Chl: chlorite, Gp: gypsum, Cal: calcite, Qtz: quartz, Ab: albite, Ge: gehlenite).

The binders of all samples mostly comprised of calcium carbonate ($CaCO_3$), confirming the calcitic matrix of the mortars (Fig. 4a). It is presumed that the calcite originated from local limestones, which were also used in the construction of the mill. The source of these limestones might be a quarry in Mitsero village, located near the mill, where reef limestones from the Koronia Member of the Pakhna geological formation are extracted [27].

In minor amounts, albitic plagioclase, along with quartz and amphibole, was detected in all binder samples. It is assumed that plagioclase and quartz are mainly derived from crushed brick [1]. The use of the latter is also supported by the presence of gehlenite within the binder fraction of all samples; this is characteristic of natural hydraulic lime burnt at temperatures < 1200°C or ceramics fired within the temperature range of 800 to 1060°C [2, 28].

Some traces of hydraulic compounds, such as portlandite, were also detected in all binder samples. Portlandite can form by slaking free lime or through the hydration of hydraulic phases. Portlandite reacts with CO_2 from the air to form calcite through carbonation. However, due to the dense structure of hydraulic mortars, part of the portlandite at the interior of a mortar may not be converted into calcite, as moisture and CO_2 cannot entirely penetrate the interior [28]. Portlandite might also be present in the samples due to the decarbonization of lime; this might be associated with certain environmental conditions, such as the humid environment of the mill [12].

Hydrocalumite was also observed in the binders of AGIM 1-1, AGIM 1-3 and AGIM 1-6. Its presence suggests the use of impure limestone and/or partially dolomitized limestones in lime production [29]. Mixing lime and dolomite with fly ash slurries results in the formation of hydrocalumite [14]. The presence of hydrocalumite in the mortars hereby studied can, therefore, be an indication that these were produced by combining lime and ashes. In sample AGIM 1-3, coal was also detected through macroscopic observations; this can justify the presence of hydrocalumite. The coal could either be a residue from the burning of limestones or could have been intentionally added to the mixture to provide hydraulic characteristics to the mortar.

Quartz, calcite, and plagioclase (albite) were the predominant phases in the aggregate fraction of all samples (Fig. 4b). Quartz is a commonly occurring mineral found in the lime mortars of many sites in Cyprus [4] and in hydraulic lime mortars from Cypriot watermills [3, 5]. Generally, quartz is associated with numerous rock types (igneous, sedimentary, and metamorphic). Therefore, in the case of the mortars under study, their origin in the river sand used might be related to the erosion of a great variety of rock types. Minor amounts of calcite and actinolite were also present in the aggregate fraction of the mortars. Last but not least, phyllosilicate minerals, such as chlorite and montmorillonite, were observed in all samples. The presence of the minerals albite, actinolite, and chlorite indicates that the sand contained an amount of material originating from lithologies of the Troodos ophiolite complex, which dominates the central part of Cyprus [27].

5 Conclusions

In this paper, four mortar samples obtained from the Vartalis watermill in Cyprus were examined. The study involved an insight into their consistency and hydraulic properties. Macroscopic and microscopic observations, along with laboratory analytical experimental techniques, such as XRD on the binder and aggregate fractions separately, as well as TG-DTA on the bulk samples, were utilized for their characterization.

The observations and analyses revealed that all four mortar samples exhibited consistency, with densely packed river sand as aggregate material and the occasional presence of lime lumps and coal. The CO_2/H_2O ratio of the samples ranged between 1.2 and 3, suggesting that these may be classified as strongly hydraulic lime mortars.

XRD analysis revealed the presence of calcite and crushed ceramic, used as artificial pozzolan, in the binder fraction and quartz and plagioclase (albite) in the aggregate fraction. The use of crushed ceramics used was likely intentional, considering their ability to provide hydraulic properties to the mortars. Furthermore, XRD analysis indicated that the river sand used contained mineral phases originating from eroded lithologies of the Troodos ophiolite. Therefore, it is evident that the raw materials utilized in the production of the mortars could be linked to the immediate environment of the watermill, as well as to the geological conditions of the wider area.

References

1. Böke, H. Akkurt, S. Ipekoğlu, B. and Uğurlu, E.: Characteristics of brick used as aggregate in historic brick-lime mortars and plasters. Cement and Concrete Research 36, 1115-1122 (2006).
2. Theodoridou, M. Ioannou, I., Philokyprou, M.: New evidence of early use of artificial pozzolanic material in mortars. Journal of Archaeological Science. 40, 3263-3269 (2013).
3. Philokyprou, M.: The beginnings of pyrotechnology in Cyprus. International Journal Architectural Heritage 6(2), 172-199 (2012).
4. Philokyprou, M.: Building materials and structures in Cypriot architecture: from the Neolithic period to the Late Bronze Age. Vol.1, University of Cyprus, Nicosia (1998).
5. Philokyprou, M.: Hydraulic mortars from watermills in Cyprus. In: Grypari, M. and Damianou, D. (eds.), Water in the traditional energy systems of the Aegean from Thrace to Cyprus, pp. 151-159. Athens (2006).

6. Kypri, G. Economides, K., Demetrakopoulos, C.: The Watermills of Cyprus. En Tipis Publications, Nicosia (2022).
7. Rizopoulou – Egoumenidou, E.: Corn-Grinding Watermills in Cyprus (18th- mid 20th centuries). In: Augusto Miranda, J. and Harverson, M. (eds.), Transactions of the 11th International Symposium of T.I.M.S. – The International Molinological Society, pp. 59-70. Portugal (2004).
8. Rizopoulou – Egoumenidou, E.: Water-powered mills in Cyprus. Recording, Research, Publication. In: Grypari, M. and Damianou, D. (eds.), Water in the traditional energy systems of the Aegean from Thrace to Cyprus, pp. 81-86. Athens (2006).
9. Department of Lands and Surveys, https://eservices.dls.moi.gov.cy/#/national/geoportalmapviewer, last accessed 2023/02/05.
10. Ventolà, L., Vendrell, M., Giraldez, P., Merino, L.: Traditional organic additives improve lime mortars: New old materials for restoration and building natural stone fabrics. Construction and Building Materials 25, 3313-3318 (2011).
11. Moropoulou, A., Cakmak, A. S., Lohvyn, N.: Earthquake resistant construction techniques and materials on Byzantine monuments in Kiev. Soil Dynamics and Earthquake Engineering 19(8), 603–615 (2000).
12. Bakolas-Karagiannis, A.: Criteria and characterization methods of historic mortars. National Technical University of Athens, Athens (2002).
13. Ponce-Antón, G., Zuluaga, M.C., Ortega, L.A, Mauleon, J.A.: Petrographic and Chemical-Mineralogical Characterization of Mortars from the Cistern at Amaiur Castle (Navarre, Spain). Minerals 10(311), 1-16 (2020).
14. Biscontin, G., Pellizon Birelli, M., Zendri, E.: Characterization of binders employed in the manufacture of Venetian historical mortars. Journal of Cultural Heritage 3, 31-37 (2002).
15. Carvalho, F. Lopes, A. Curulli, A. Silva, T.P. Lima, M.M.R.A. Montesperelli, G. Ronca, S. Padeletti, G., Veiga, J.P.: The case study of the Medieval town walls of Gubbio in Italy: First results on the characterization of mortars and binders. Heritage 1, 468-478 (2018).
16. Moropoulou, A., Bakolas, A., Bisbikou, K.: Investigation of the technology of historic mortars. Journal of Cultural Heritage 1, 45-58 (2000).
17. Bonnerot, O., Ceglia, A., Michaelides, D.: Technology and materials of Early Christian Cypriot wall mosaics. Journal of Archaeological Science: Reports 7, 649-661 (2016).
18. Moropoulou, A., Bakolas, A., Bisbikou, K.: Characterization of ancient, byzantine, and later historic mortars by thermal and X-ray diffraction techniques. Thermochimica Acta 269/270, 779-795 (1995).
19. Alvarez, J.I., Navarro, I., Garcia Casado, P.J.: Thermal, mineralogical and chemical studies of the mortars used in the cathedral of Pamplona (Spain). Thermochimica Acta 365, 177-187 (2000).
20. Arizzi, A., Cultrone, G.: Aerial lime-based mortars blended with a pozzolanic additive and different admixtures: A mineralogical, textural and physical-mechanical study. Construction and Building Material 31, 135-143 (2021).
21. Meréndez, E., Vega, L., Andrade, C.: Use of decomposition of portlandite in concrete fire as indicator of temperature progression into the material. Application to fire-affected builds. Journal of Thermal Analysis and Calorimetry 110(1), 203-209 (2012).
22. Moropoulou, A., Bakolas, A., Aggelakopoulou, E.: Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis. Thermochimica Acta 420, 135-140 (2004).
23. Corti, C. Rampazzi, L. Bugini, R. Sansonetti, A. Biraghi, M. Castelletti, L. Nobile, I., Orsenigo, C.: Thermal analysis and archaeological chronology: The ancient mortars of the site of Baradello (Como, Italy). Thermochimica Acta 572, 71-84 (2013).
24. Bakolas, A., Biscontin, G., Moropoulou, A., Zendri, E.: Physico-chemical characteristics of traditional mortars in Venice. Transactions on the Built Environment 15, 187-194 (1995).
25. Bakolas, A., Biscontin, G., Moropoulou, A., Zendri, E.: Characterization of structural byzantine mortars by thermogravimentric analysis. Thermochimica Acta 321, 151-160 (1998).
26. Ingo, G.M., Fragala, I., Bultrini, G, Caro, T., Riccucci, C., Chiozzini, G.: Thermal and microchemical investigation of Phoenician-Punic mortars used for lining cisterns at Tharros (western Sardinia, Italy). Thermochimica Acta 418, 53-60 (2004).
27. Fournari, R. Ioannou, I.: Correlations between the Properties of Crushed Fine Aggregates. Minerals 9(86), 1-22 (2019).
28. Callebaut, K. Elsen, J. Van Balen, K., Viaene, W.: Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium). Natural hydraulic lime or cement?. Cement and Concrete Research 31, 397-403 (2001).
29. Ponce-Antón, G. Ortega, L.A. Zuluaga, M.C. Alonso-Olazabal, A., Solaun, J.L.: Hydrotalcite and Hydrocalumite in Mortar Binders from the Medieval Castle of Portilla (Álava, North Spain): Accurate Mineralogical Control to Achieve, More Reliable Chronological Ages. Minerals 8(326), 1-17 (2018).