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Characterisation of Ancient Gypsum Mortars from the Archaeological Site of Amathus, Cyprus

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Abstract The purpose of the present research work was the mineralogical, mechanical and microstructure characterization of the gypsum mortars sampled from the internal parts of the crepis (foundation) of the Aphrodite temple and the walls of the early Christian basilica from the archaeological site of Amathus, Cyprus. The project is part of the studies carried out by the French Archaeological School of Athens in view of a possible anastylosis of the temple. The tests included (a) wet chemical analysis for the oxide determination, (b) XRD analysis, with nickel-filtered CuKα radiation, (c) TG/DTA analysis in the range of 25-1000°C, (d) scanning electron microscopy coupled with microanalysis, (e) optical microscopy performed in thin sections in transmitted light and (f) mechanical tests for the determination of the tensile strength. The examined binders were composed by hydrous calcium sulphate (CaSO₄·2H₂O) and small proportion of CaCO₃ and SiO₂, whose detection was attributed to their presence in the initial mineral gypsum.

1 Introduction

Amathus was one of the most ancient royal cities of Cyprus, on the southern coast, about 24 miles west of Larnaca and 6 miles east of Limassol. The ancient city of Amathus was inhabited since the 11th century B.C. and destined to become one of the leading states of the Cypriot Iron Age, no less powerful and prosperous than the Greek city kingdoms. It was a rich and densely populated kingdom with a flourishing agriculture, and it was important because of its port, from where it exported copper and timber. In the Roman era it became the capital of one of the four administrative regions of Cyprus. The dominant feature at Amathus is its acropolis, the upper city. The easily fortified hill was undoubtedly the site of the
original settlement and the home to the great goddess who protected it. Her original name is unknown, but by Classical times she was firmly identified with Aphrodite. In Late Antiquity (3rd-7th centuries AD), the temple was replaced by an early Christian basilica, but little remains apart from the foundations. Excavations in the area began in 1980 and continue by teams of Cypriot and French archaeologists, bringing to light the Acropolis, the temple of Aphrodite, the Market, the city’s Walls, the Basilica, and the Port.

The study of ancient mortars is of great importance from an archaeological and technological point of view. Ancient mortars are an important source of information, and their analysis may give an indication of the composition of mortar mixtures used during the different periods, as well as their state of preservation. Mud, gypsum, and lime had traditionally been the three most common binder types during the construction history of mankind [1]. The binder glues aggregates and other particles together and provides adhesion to the substrate. Due to their physical or chemical reaction, binders play the major role in the final strength of the mortar.

Gypsum is a relatively easily mined rock, chemically known as hydrous calcium sulphate. When heated to approximately 130°C, part of the water is driven off according to the reaction

\[ 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow (\text{CaSO}_4) \cdot \frac{1}{2}\text{H}_2\text{O} + 1.5\text{H}_2\text{O}. \]

When recombined with water, an interlocking crystalline structure of hydrous calcium sulphate \((2\text{CaSO}_4 \cdot 2\text{H}_2\text{O})\) is re-established. The structure is made up of sheets of \(\text{Ca}^{2+}\) and \(\text{SO}_4^{2-}\) ions held together by hydrogen bonds in the water molecules.

The oldest use of burnt gypsum occurred in dynastic Egypt from 5000 to 3400 B.C. It was used along with Nile mud as mortar during building and as plaster of walls and floors in tombs [2]. About 2000 BC, the ancient Minoans built a sandstone-paved road extending from the southern to the northern coast of the island of Crete. The mortar used to affix the sandstone pavement was a clay/gypsum mixture [3]. It also was used in other countries in the Middle East and in medieval times for masonry mortars in the region around Lübeck in Northern Germany [4] and in the Paris region. In many cases, gypsum mortars placed between the carefully squared stone blocks were not actually used as joints, but mainly as filling material in order to accurately arrange stone blocks on the structure.

The use of gypsum in construction was known in Cyprus since Prehistory. Abundant reserves of this mineral are found in Cyprus and are nowadays an important product for export. Gypsum belongs to the geological formation of Kalavasos. In Cyprus, gypsum appears as laminated, i.e. in thin alternating layers, as laminated with concretions, and as selenite with twin crystals [5].

Chemical examination of ancient gypsum mortars by Lucas [6] has shown that the ancient Egyptians never used lime until the Roman Period. Lucas explained
that gypsum was preferred over lime because of the scarcity of fuel. Gypsum was generally quarried in a very impure state and usually contained calcium carbonate. He also stated that the gypsum used was often impure and contained natural admixtures of calcium carbonate and quartz sand. Ghorab et al [7] analysed, by XRD, samples from the Gizeh Pyramids and from the Sphinx. The minerals identified were gypsum, anhydrite, calcite, and silica. Gypsum was predominant in the Sphinx. According to Regourd [8], the Cheops and Unas pyramids were built in 2500 and 2250 BC with mortar in which gypsum microcrystals occur as the product of the anhydrite transformation. Sabnis and White [9] found that the ultimate strength of gypsum mortar is based largely on the water-to-gypsum ratio and on the aggregate-to-gypsum ratio. They report that increasing the aggregate ratio from zero to 1.2 reduced compression strength by up to 50%. An increase in water ratio from 0.3 to 0.4 also reduced compressive strength by 27-34%.

2 Experimental

In order to obtain information about the Amathus mortars’ composition, mortar samples were smoothly separated and sieved through ISO 565 series of sieves. This enabled estimation of the proportions of binder/aggregate within the mortar. The most significant fraction of the grain-size distribution, for the aim of this research, is that of <63 μm consisting mostly of the binder.

Chemical analysis of the principal components was carried out by attack with a sodium carbonate-borax alkaline flux and the subsequent analysis of the elements by traditional chemical methods.

The mortars’ binders were characterized by a Nicolet 560 IR Magna Fourier transform spectrophotometer, in the range of 4000-400 cm\(^{-1}\) with 200 successive scans. The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector and with an attenuated total reflectance (ATR) unit. The spectra rationed against a potassium bromide (KBr) background. The ATR sampling compartment is a ZnSe crystal (refractive index 2.4) with an angle of incidence of 45° oriented horizontally. The size of the rectangular surface area of the ATR crystal is 60 mm \(\times\) 10 mm.

Mineralogical analysis was carried out by X-ray diffraction (XRD), using a Bruker D8-Focus diffractometer with nickel-filtered CuK\(\alpha\)1 radiation (=1.5405 Å), 40 kV and 40 mA.

TG/DTA analysis was conducted with a Setaram-Labsys thermal analyzer. Type S-thermocouple is used for temperature measurements in this instrument. The sample was placed in a ceramic crucible and heated from room temperature to 1200°C at a heating rate of 5°C/min using air as a medium under static condition. TG/DTA were done simultaneously.

The fragments-test method was used to estimate the tensile strength of the ancient mortar [10]. For that purpose, the installation of the Laboratory of
Reinforced Concrete at the NTUA was used. A small specimen of 40 mm x 20 mm x 28 mm was cut from the original piece, glued in a special mould using a strong epoxy resin, and subjected to direct tension.

Optical microscopy was performed on thin and polished sections. Thin sections were produced by vacuum impregnation of the selected sample with epoxy resin, followed by cutting, grinding, and polishing, until a final thickness of 20 \( \mu \)m was reached.

The microstructure of the mortar samples was evaluated by scanning electron microscopy (SEM) using a Jeol 6380 LV SEM. Experimental conditions involved 20 kV accelerating voltage using a backscattered electron detector. SEM was performed in polished sections. Microanalysis was performed by an Oxford INCA Energy Dispersive Spectrometer (EDS) connected to the SEM.

### 3 Results and Discussions

All the examined mortars presented a very dense structure, making the crushing process very hard. The direct tension test revealed a quite high value of tensile strength \( f_{tu}= 1.93 \text{ MPa} \). The mortars’ apparent porosity was found equal to 25.3%.

The detected aggregates were very fine and they did not present well-defined edges. The chemical analysis of a typical mortar binder is given in Table 1.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>K(_2)O</th>
<th>Na(_2)O</th>
<th>SO(_3)</th>
<th>LOI(_{1000})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>1.07</td>
<td>0.14</td>
<td>0.10</td>
<td>37.40</td>
<td>0.48</td>
<td>0.34</td>
<td>0.68</td>
<td>31.88</td>
<td>11.21</td>
</tr>
</tbody>
</table>

The examined mortars’ binders are mainly composed of up to 38% of CaO and up to 32% of SO\(_3\), whereas loss of ignition at 1000°C is in the range of 11%-12%. The measurements also showed that silica and aluminium/iron oxide are found in very small proportion, rather as impurities and not as part of the binder. As a result, it is a gypsum mortar, which contains about 68.5% of CaSO\(_4\) \(_{2\text{H}2\text{O}}\).

The results of chemical analysis were confirmed by the mineralogical analysis. The X-ray diffraction pattern of a typical mortar binder is presented in Fig. 1. The presence of principal reflections at the d-spacings 7.5900, 4.27885, 3.0613, 2.8754, and 2.6830 Å and their intensity confirmed that the major phase of the sample is gypsum. The additional weak reflection occurring at the d-spacing 3.0289 Å also indicated the presence of a small amount of calcium carbonate. No detectable amounts of bassanite or anhydrite were present.
As mentioned above, the binder was produced after a thermal treatment (130-170°C) of mineral gypsum, which is dehydrated partially in order to produce hemi-hydrate. During hydration, hydrous calcium sulphate (CaSO$_4$.2H$_2$O) is re-established. The detection of CaCO$_3$ (10%) should be attributed either to the remains of the fine calcareous aggregates in the binder or to the presence of calcite as an impurity in the initial mineral gypsum.

TG-DTA analysis results are in agreement with XRD data. Fig. 2 illustrates removal of hygroscopic water at 100°C, followed by the water of crystallization during the transition to the hemihydrate form. The endothermic peak at 165°C, relates to the loss of 1.5 molecules of water from CaSO$_4$.2H$_2$O. The second endothermic peak at 190°C represents the loss of the remaining 1/2H$_2$O during the formation of CaSO$_4$. The exothermic peak at 380°C corresponds to the phase transformation from soluble to insoluble anhydrite. A small endothermic peak was also detected at 800°C, which was attributed to the presence of calcite (previously observed by XRD). Carbonates show distinctive endothermic peaks, whose position may vary depending on grain size, atmosphere, and other concomitant factors. They are due to the escape of CO$_2$ during the breakdown of their structure. Continued heating above 1100°C reduces the insoluble anhydrite to CaO and sulphur trioxide gas (SO$_3$).
Fig. 2 T.G. and D.T.A. analysis of a typical mortar binder

Fig. 3 FT-IR spectra of the examined mortar binder

Fig. 3 presents the FT-IR spectra of a typical mortar binder. The observed bands in the area of 3500 cm\(^{-1}\) attest the presence of water of crystallization. The \(\nu_3\) and \(\nu_1\) H\(_2\)O vibrations are detected near 3620 and 3400 cm\(^{-1}\), but sometimes depend on the degree of hydrogen bonding in the mineral lattice. The two water-bending vibrations are observed at 1620 and 1682 cm\(^{-1}\). The absorption taken
from the area of 1100-900 cm\(^{-1}\) corresponds to vibration of valence O-S. Fundamental sulphate vibrations occur for the sulphate ion due to symmetric (\(\nu_1, 981 \text{ cm}^{-1}\)) and asymmetric (\(\nu_3, 1104 \text{ cm}^{-1}\)) stretching. A strong doublet is observed near 600 and 670 cm\(^{-1}\) due to the \(\nu_4 (\text{SO}_4^{2-}\)) bending vibrations. The weak band at 1460 cm\(^{-1}\) indicates the presence of carbonate species in the sample.

The morphology of the examined gypsum mortars and their association with calcite and quartz sand was observed under OM and SEM (Figs. 4, 5).

![Fig. 4 Thin-section observation of the mortars. Gypsum matrix with calcite-quartz inclusions](image)

![Fig. 5 SEM micrographs. Matrix of gypsum idiomorphic crystals with calcite-quartz inclusions](image)

The white micritic calcite inclusions, as well as those of quartz, were easily distinguished in optical microscopic analyses. Analysis of the mortars by SEM/EDS showed that all mortars have a compact microstructure. Gypsum is the
most abundant phase. A tightly intertwined network of well-formed idiomorphic crystals and flaky particles made up of small crystals (10-20 μm) is observed. Nevertheless, the presence of microscopic cracks was noticed. These cracks were attributed to the initial shrinkage of the mortar. The porosity consists of small, interconnected pores with approximately 1 μm size and large spherical pores (>50 μm) formed by trapped air in the initial raw material powder. Calcite and quartz were observed in low proportion as inclusions inside the gypsum of matrix. Both inclusions did not present well-defined edges, a fact that confirmed the absence of crushed aggregates added in the initial mortar.

4 Conclusions

The mineralogical, mechanical, and microstructural characterization of the gypsum mortars sampled from the internal parts of the crepis (foundation) of the Aphrodite temple and the walls of the early Christian basilica from the archaeological site of Anathus, Cyprus, reveals that they are made of gypsum, which contains natural admixtures of calcite and quartz. Gypsum forms a tightly intertwined network of well-formed idiomorphic crystals and flaky particles made up of small crystals and shows a quite high tensile strength. Calcite and quartz were observed as inclusions, with not well-defined edges inside the gypsum matrix.

5 References