Analysis and Conservation of Ancient Egyptian gypsum-based binders and mortars from the temple of Ramesses II in Antinoe
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1. Introduction
This study is carried out in collaboration with the Italian Archaeological Mission in Antinoe, within the program of surveys and research for the preservation of the Temple of Ramesses II. The project aims to improve the current level of knowledge on the materials employed in the temple complex through an interdisciplinary analytical approach. A long-term and broader goal is the development of guidelines for the characterization, diagnosis, selection of compatible materials for restoration and establishment of procedures for conservation and sustainable maintenance. The results can help to provide a clearer picture of some materials used in architecture during the Ramesside era. This phase of research focuses on the characterization of the gypsum-based binders.

2. The use of gypsum as binder in pharaonic buildings
The constructive culture of Pharaonic Egypt is characterized by the production of binders obtained from the firing of sulphate rocks¹. The low-temperature processing is undoubtedly one of the main driving factors. At temperatures as low as 110-160° C calcium sulfate dihydrate (CaSO₄·2H₂O) loses water and turns into hemihydrate (bassanite, CaSO₄·½ H₂O) in two forms α and β. Between 170°-300° C, the dehydration is complete and anhydrous gypsum or soluble anhydrite (CaSO₄) appears. Both processes are reversible and the compounds obtained can be easily rehydrated. At over 300° C the transformation of anhydrite into the insoluble form occurs, producing a stable and little hydratable material, which is completed at 500° C. Between 900° and 1100° C free lime (CaO) appears. The addition of water to the hemihydrate and anhydrite causes, in a few minutes, the formation of long thin crystals of dihydrate gypsum, twisted in a fibrous and compact mass. The anhydrous irreversible form takes a much longer time to set and harden. The Egyptian workers were aware of how the quality of the raw material and the methods of firing can affect the characteristics of the final product. Undoubtedly they took into account these factors for the preparation of different types of mixtures according to their function in the building²: mortars for laying stone blocks, mortars for compact and durable coating plasters, to be carved or exposed outdoors³; fluid mixtures applied by brush in preparation of the painted decoration⁴.

2.1. The study of pharaonic mortars
Among the first scientific studies are those carried out by Alfred Lucas⁵ in 1926, who confirmed the gypseous nature of Pharaonic mortars and their variable composition. The steady increase of case studies over the years has
improved the knowledge of these materials and has clarified several aspects of the methodology needed for their characterization, outlining the complexity of materials.\textsuperscript{6} The heterogeneity of these binders and their frequent alteration and degradation require appropriate modifications of laboratory tests for proper characterisation.\textsuperscript{7} Consolidated mineralogical and chemical analysis (LOM, XRD, SEM, MIP), are not always sufficient. Moreover, many standard procedures applicable to lime-based mortars, are not systematically transferred to those based on gypsum. The effectiveness of the investigation is often determined by the juxtaposition of multiple methodologies.\textsuperscript{8} Current studies increasingly include the analysis of degradation, the development of conservation procedures and compatible materials for restoration.\textsuperscript{9}

3. The mortars of the Ramesses II’s temple in Antinoe

Built by Ramses II in the 13th century B.C.E., the temple has been enriched with decorations by pharaohs of the Nineteenth and Twentieth dynasty. Incorporated in the city of Antinoe, founded by Emperor Hadrian in 130 C.E., it has been slowly abandoned, with the first collapses and spoliations, in late antiquity. Currently the temple is part of the archaeological area, near the village of el-Sheikh Abadah (el-Minya district). The larger part of the remains consists of 20 columns, 14 of the courtyard and 6 of the hypostyle hall. Of great interest is the modeling technology of the shaft which involved the use of mortar for the specific integration of the stone volumes.\textsuperscript{10} In order to simulate the sandstone, this process was refined with the use of several overlapping layers of mortar, forming an artificial material to be carved after hardening. The extensive collection of mortars and traces of actions, stratified in the temple of Antinoe, are a valuable document for understanding its evolutionary phases and, more generally, pharaonic construction technology. Preliminary investigations (statistic and typological) on macroscopic characters allowed the identification of 12 different types of mortar\textsuperscript{11}: mortars for laying of blocks (5), inner integration plasters (3), outer coating plasters (4). Stratigraphic investigations link the mortars and plasters to the Ramesside construction phase and the preparatory layers to the later interventions of decoration. Standard technological procedures have been identified together with specific solutions of the construction and decoration actions. The processing of data obtained has highlighted the most representative portions for the careful collection of micro-samples (fragments or powder). Priority was given to the already detached fragments.

3.1. Analytical methodologies

A preliminary characterization of the material samples was carried out on polished micro-fragments, cross-sections and thin sections, by means of optical microscope (LOM). The mineralogical composition was determined by X-ray powder diffraction analysis (XRD).\textsuperscript{12} Chemical analyses were carried out following the instructions of some UNI standards to determine the insoluble residue of acid attack (siliceous and/or silicatic aggregate), the soluble species and the mass loss at various temperatures (UNI11088), the CO\textsubscript{2} content (UNI 11140), useful to assess the presence of carbonates, the total content
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General view of the temple from the South. On the left the remains of the courtyard. On the right the columns of the hypostyle hall of free lime and magnesia (UNI11139). Porosimetric analysis were performed with Mercury Porosimeter (MIP), on fragments of the central portion after mechanical separation carried at the stereo-microscope. Some samples were analysed with Fourier Transform Infrared Spectrophotometry (FT-IR). The micro-structure and the chemical composition were investigated by means of scanning electron microscope (SEM) equipped with an energy-dispersive X-ray detector (EDS).

4. Results and discussion

All mortars investigated have a gypsum-based binder. Substantial differences are mainly due to the variable presence of anhydrite in the binder, the compactness and porosity, the type and amount of aggregate. These variability factors seem to be associated with the functions of these mortars, (for laying blocks or for coating surfaces) but also to the location in the building, a clear sign of the different phases of construction and materials production. One of
the most significant results is the constant presence of a very fine part of the aggregate (10-50 μm), consisting exclusively of carbonate crystals, distinct from the main aggregates (100-1000 μm). These fine particles may be the finest residual of grinding of limestone or the unfired calcareous part of the gypseous rocks. We cannot exclude that the stone to be fired was also chosen because of its mixed calcareous-gypseous composition, since the presence of carbonate slows the setting and hardening times, favoring building work.

4.1. Mortars for laying blocks
In the columns of the courtyard, mortars between blocks of the shaft are characterized by a binder with a high content of anhydrite (detected by XRD but not in thin section) and completely devoid of dihydrate gypsum. Anhydrite may have been the main component of the gypseous rock used or the product of the dihydrate (selenite) firing, to more than 500 ° C. Even in the aggregate, which is calcareous and silicatic, gypsum was not detected. The carbonate part is composed of rock fragments and crystals of spathic calcite. A high content of halite (NaCl) has been detected, probably related to the nature of the evaporitic rocks used. In the terrace (columns and entablature), the binder of mortars consists of gypsum dihydrate (anhydrite is absent). The aggregate is mixed, consisting of silicates, gypsum crystals or rock fragments and a carbonatic part, consisting only of rock fragments (often fossiliferous), comparable with the local formations. In all these connection mortars the binder/aggregate ratio varies from 1/1 to 2/1. It is indicative of a rich lime mixture, likely to reduce friction during the laying of the blocks.

4.2. Plaster layers
Because of their wide distribution in the building, the coating plasters are the most heterogeneous group of mortars. The inner layers are the most various in characteristics and amount of aggregate and binder. Gypsum, detected in the binder, is low or totally absent in the aggregate, mainly calcareous and silicatic. The outer coating plasters are more compact and tough compared
to the underlying layers. They tend to be white, with localized areas of heterogeneous porosity and structure. The chemical analysis confirm gypsum as binder and a constant presence of anhydrite. The absence of free lime would exclude firing temperatures higher than 900° C. The aggregate is composed of quartz and fragments of calcareous rock, often fossiliferous. Spathic calcite, constantly detected in mortars for laying of blocks, is completely absent. In addition to these components, there’s also gypsum, such as crystals and fragments of rocks. The binder/aggregate ratio is higher compared to the underlying integration layers, with the likely purpose of increasing the plasticity during modeling. In the outer coating plasters of the lateral colonnades of the courtyard, the amount of fine carbonate crystals (<50 μm) in the aggregate exceeds, in terms of quantity, that of the gypseous binder. This characteristic has never been observed in mortars for laying of blocks. Outer plasters from the entrance colonnade of the temple are distinguished by the high concentration of anhydrite in the binder and the smaller particle size of the aggregate (50-650 μm). The analysis by SEM-EDS shows the structure of these outer coating plasters, with the grains of quartz, calcite and gypsum of the aggregate surrounded by small crystals of gypsum (binder) and calcite. The porosity is around 30%, with pore sizes ranging between 0.1-1.0 μm and 3.5-16 μm in diameter. The shape of pores is irregular and heterogeneous. In some cases it seems the result of poor mixing, in others it may be the product of alteration and deterioration of the binder. The two superimposed layers of plasters in column 5 are very similar in composition. This suggests that the building phases of plastering and final modeling have been performed in a fairly narrow temporal range for each of the columns.

4.3. Preparatory layers for paintings
The thin under-layers, applied in preparation for the painting, are the most uniform, fine and white. Only gypsum and quartz have been detected by XRD analysis. The absence of carbonates indicates that the production of the binder was not linked to rocks with a mixed composition (carbonate-gypsum). Depending on requirements, workers were able to obtain high quality gyp-
sum, which was virtually pure. The type of aggregate, made exclusively of fine quartz (50-250 μm), can help in confirming the wide range of available materials and the careful selectivity of the foremen. These preparatory layers were made by teams of decorators, distinct from those who worked on the construction and modeling of the columns.

5. Conclusions and perspectives
The analytical campaign allowed the identification of the chemical composition and the structure of these materials. Some assumptions have been outlined, about production and processing criteria. Many questions remain open and are currently being investigated. Having recognized the gypseous nature of the binder it is necessary to investigate how its composition is directly influenced by that of the original sulphatic rock and by the firing. Another key issue to be addressed is the presence of carbonatic aggregate that does not allow to calculate chemically the binder/aggregate ratio. This entails the development of an appropriate procedure, which must consider the presence of water-soluble or acid-soluble minerals (CaCO₃, NaCl, etc.). The role of the fine crystalline part (<50 um) of the calcareous aggregate during the steps of setting and hardening is not clear. The degradation phenomena are due mainly to natural factors and, in small part, to the occasional human actions. Humidity and temperature variations have been seasonally monitored. Combined with the chemical and morphological characteristics of mortars, they can accelerate degradation, especially in the most exposed and vulnerable
portions of plaster finishes. The mechanical action of the wind causes widespread erosion and accumulation of fine material on the surfaces. Investigated by SEM, this thin layer of deposit (<1 mm) is made up of a dense mass of granules of clay minerals, gypsum and quartz. A program of analysis has started to identify any organic compound added as an additive to mortars and painting mixtures, applied as a surface treatment or produced by alteration.

Notes

1. The main deposits of gypsum in Egypt are found near Alexandria, Port Said, Fayoum and on the Red Sea coasts (Gulf of Suez, Qoseir, Ourghada). They are formations of calcium sulfate dihydrate \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \), often mixed with anhydrite \( \text{CaSO}_4 \). It is not excluded that other formations in the country, thin layers of gypsum alternated or mixed with varying amounts of impurities (clay, sodium chloride, etc), were exploited.

2. The insoluble anhydrite detected in some mortars of the temple of Amun at Karnak (Martinet, 1992) has been linked to the production of a low-setting binder that favored the blocks to slide during the laying. This seems to be confirmed by the absence of the anhydrous form in the coating plasters, where prevails the dihydrate.

3. A more or less articulated sequence of layers was applied on the surface. The inner coarse layers, with leveling functions, and the outer ones most selected, refined and compact (Nicholson, 2009, pp. 117-118). Even the use of mixtures of clay was very common, but mostly limited to interiors, such as the tombs.

4. This layer was used to correct the imperfections and smooth the surface, especially in the case of a mixed support, little compact or heterogeneous. It avoided uncontrolled absorption of color by the stone or plaster. It was smoothed still wet and colored after drying (Goyon, 2004, p. 358-360). Cases in which the tempera painting was applied directly on the stone, are not uncommon (Marey Mahmoud, 2011 p. 101).

5. The results show highly variable compositions. Gypseous component, from a minimum of 23% goes up to 90%, while the carbonate content is between 0.7% and 71% of total (Lucas, 2003 - p. 230).

6. Among the numerous studies, there are those conducted at Djehuty (Sanchez Moral, 2011), el Qurna (Marey Mahmoud, 2011), Karnak (Martinet, 1992), Giza (Nakhla 2006) e Abydos (Liritzis, 2008).

7. It is very useful, for example, to determinate the ratio between soluble and insoluble \( \text{CaSO}_4 \) (Martinet, 1992) or to establish the difference between binder and aggregate of identical chemical composition (Deloyé 1991, Casadio, 2005).

8. Studies carried out by a team of the University of Aegean, on some materials of Abydos and Giza, have included XRF tests, analysis of the radioisotopes content, optoluminescence for dating the blocks (Liritzis, 2008).

9. Investigations carried out on mortars of the Sphinx of Giza (Nakhla, 2006) and on the stone materials of temple complexes at Karnak and Luxor (Fitzner, 2003).

10. In its simplest form this procedure can be found in some Ramesside specific interventions in the mortuary temple of Sethi I at Qurna (Marey Mahmoud, 2011) and in the temple of Amun at Karnak (Rondot, 1997). The major similarities with this type of work seem to be found in the traces of the actions promoted by Sethi I in the columns of the temple of Sesebi in Sudan (Fairman, 1938).

11. For example, two main types of mortars for building the shaft have been identified, different between the two lateral colonnades and that of the front.

12. Analyses were carried out at the Department of Earth Sciences, University of Florence, on behalf of the Istituto Papirologico “G. Vitelli”, which has kindly provided the
results.

13 Chemical tests were carried out at the Materials Testing Laboratory of the Department of Civil and Environmental Engineering (DICA) of Politecnico di Milano.
14 Analyses were carried out at the LAM (Stone Materials Analysis Laboratory) of the Department of Earth Sciences – University of Florence.
15 Analyses were carried out at the Department of Chemistry of the Politecnico di Milano.

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