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ANCIENT GYPSUM MORTARS FROM St. ENGRACIA (ZARAGOZA, SPAIN): CHARACTERIZATION. IDENTIFICATION OF ADDITIVES AND TREATMENTS

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ABSTRACT

The ancient mortars coming from the alabaster main façade of the St. Engracia Basilica (XVI century). The research has been carried out about the original joint mortars and the repairing mortars of several restorations. The characterization of different types of mortars was made by the application of optical microscopy, scanning electronic microscopy with EDX, X-ray diffraction, infrared spectroscopy and laser granulometry. Gypsum is the main component. There has been studied on the mortars: the composition, the binder/aggregate ratio, the granulometry of the binders and the aggregates, and the identification of the additives (organic compounds,..) used in the mortars. The design of the restoration mortars has been achieved by the knowledge of the studied mortars.

Introduction

One of the main problems in the restoration or conservation of a monument is the knowledge of the composition of the ancient mortars and the additives they have. Although this knowledge is vital to make a good intervention on the monument.

A systematic study applied to the several mortars found in the alabaster façade of the St. Engracia Basilica has been made in order to design suitable mortars for the restoration, according to compatibility methods with the found ancient mortars.

It has been taken into account that in the investigation of monument mortars the first problem is their possible heterogeneity caused not only by their function to carry out as materials in the building, but by the different interventions and periods in which they were produced and the consequent difference of techniques and traditions to consider in their study and the possible degradation of the mortars due to the time passed.

There has been considered the existence of other kinds of methodology, as the one proposed by H. Jedrzejewska (1),.widely extended for its simplicity, used for the classification of the mortars by its typology and to distinguish them from the hydraulic characteristics of the mortars (2), but it only provides a semi-quantitative analysis and it starts with the grounding of the mortars, followed by the attack of chlorhidric acid of the

traditional analysis (3). By the othe hand, M. Frizot (4) thinks that the analysis of the mortars has to be made in a global point of view.

The systematization of this research can be applied to the study of other monuments. It has been taken into account that the ancient mortars were usually prepared with a mixture based on water, binding material and some specific aggregates and eventually some additives of different nature with the aim of modifying some of their characteristics. For that reason, in the study made it has been considered the characterization and identification of the binder, the aggregates, its relative proportion and the existence of additives.

HISTORY: The main façade of St. Engracia Basilica was conceived as a retable by its author Gil de Morlanes (1504). Made up of alabaster coming from the quarries of Bajo Aragón (Velilla).The façade was highly transformed in the XVIII century due to the ruin threat which had the building and loss of the mortars as well as displacement of the side columns. During the Independence War (1808) the façade remains seriously spoiled. There is proof on an intervention made in 1857. In 1878 a lightning falls over the bell tower causing again damages. In 1887 M. López carries out a first restoration project in which reinforces the most spoilt.

C. Palao presents a wider intervention project in 1894, restoring the whole of the façade and the replacement of some of the figures. He accomplished different interventions placing alabaster plugs in the damaged areas by the shrapnel and completing with alabaster, with plaster mortar and polychrome plaster of Paris. He also made a filling inside of the joints as well as some of the cracks. Finally he applied on the whole façade a protecting coat with calcium sulfate (5), probably with the aim of matching the chromatic differences among the original alabaster and the replacements. Around 1974 there is proof of a new intervention by Albareda brothers, who removed the accumulated deposits of pigeon excrements and applied a protecting and waterproof coating with mineral oil (5).

Besides, it is possible that in the XVIII, XIX and XX centuries the basilica could experiment other interventions because of its great diversity of repairs with mortars found in the façade and cramps and iron rods. The right leg of Christ figure has suffered from several breaks with the consequent giving off of the repair mortars. It would be surely removed any time too. Some specific reintegrations have been found with several mortars. In 1993 it was accomplished a new restoration which corresponds to the investigation on mortars carried out by the present work.

Experimental

MORTAR SELECTION: In the restoration study have been considered:

* Joint mortars: It is thought that the outer part of the jointings correspond to possible restorations and will probably be more recent whereas the inner ones will provide old mortars. The specific study of such mortars will give the necessary information to prepare the mortars for the intervention.

* Several mortars corresponding to different repairs accomplished in various places of the façade. They constitute independent samples.

In the study of samples, previous mortars and later mortars to Palao intervention, Groups: P and L, have been distinguished, as well as samples coming from others

restorations and repairs (Group R). The results of a selection of mortars between the variety of studied mortars is shown in the Table 1.

TABLE 1.- Mortar Selection

GROUP	SAMPLE	DESCRIPTION
P	F	Interior mortar - Vertical joint (Width ≅ 3 cm)
P	J	Interior mortar - Vertical joint (Width ≅ 3 cm)
P	O	Interior mortar - Horizontal joint (Width < 1 cm) - FIG. 1
L	G	Exterior mortar - Vertical joint (Width ≅ 3 cm)
L	S	Exterior mortar - Vertical joint (Width ≅ 3 cm)
L	W	Exterior mortar - Horizontal joint, S. Gregorio (Width ≅ 3 cm)
R	K	Repairing mortar, from right leg of Christ figure
R	L	Repairing mortar, from right ankle of Christ figure
R	P	Repairing mortar, from Santa Paula figure's sleeve - FIG. 1
R	T	Repairing mortar, from a re-engraved alabaster piece - FIG. 2
R	X	Repairing mortar, from hollow of an anchorage (S. Lamberto's)
R	Y	Joining mortar of the above mentioned piece, from Palao period

FIG. 1.- Sampling of O Joint Mortar and Repairing P Mortar

METHODOLOGY: Each sample has been studied as a whole through the observation by optical microscopy, scanning electron microscopy (SEM) with X-ray energy microanalysis (EDX) and infrared absorption spectroscopy (IR). Afterwards, the aggregate and the binder have been separated to make the physical, chemical and mineralogical characterization of both components separately by using the techniques: sieving, SEM / EDX, X-ray diffraction (XRD), thermal analysis, extraction and analysis with chloroform-ethanol processing, laser granulometry (LG). The analysis of each of the mortars was based on the available quantity of sample and the final test objective.

Results and Discussion

P (prior) and L (later) MORTAR GROUPS: The characterization of both groups of mortars is comparatively carried out.

The visual samples observation was made through optical microscopy. In the old J mortar ochre and reddish tone aggregates of clayey shape were found whereas in the same area

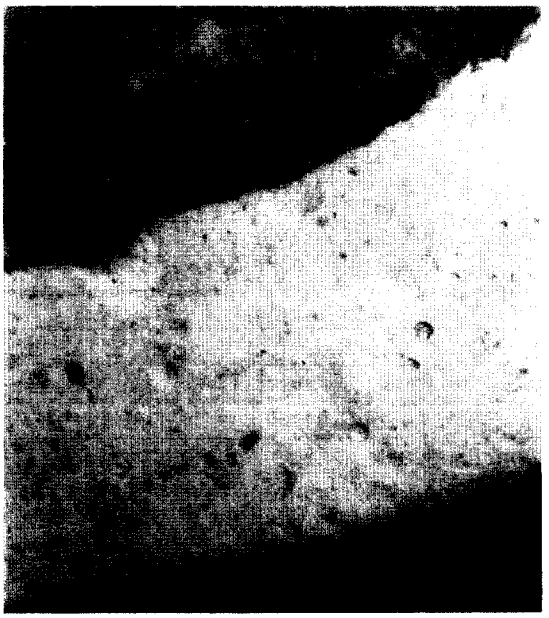

FIG. 2.- Reconstitution Mortar of the Re-carved T Piece (x 10,7)

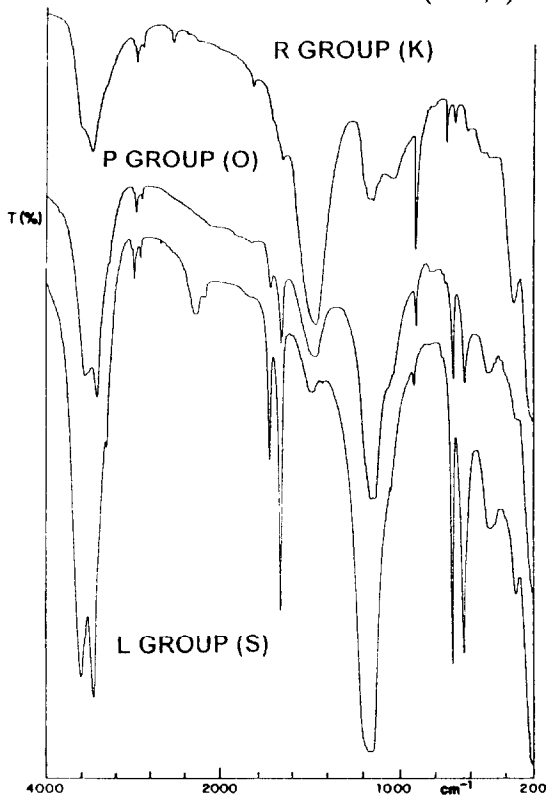

FIG. 3.- IR Spectra of Mortars

the S mortar, later to the building, presents a similar appearance to that of the reconstitution mortar of the re-carved T piece (FIG. 2), that presents a good conservation state and good adherence with the alabaster, and it is like G mortar. In the W sample, extracted as coming from the Palao restoration period, two areas can clearly be distinguish: the inner one which contains small wood particles constituting part of the mortar mass and conferring more resistance to it and the outer coat formed by a gypsum base without aggregate and a protecting coat covered by dirtiness.

The application of IR spectroscopy corroborated the classification of P Group, because J and O mortars seem very similar between them. In their IR spectra (FIG. 3) there are gypsum, carbonates (dolomite), absorption in the silicate area (vibrations Si-O-Si); in the same way, these mortars are similar to F sample in which apart of that, it are detected nitrates.

In this sense, in L Group samples G and S are very similar because they are almost constituted in the whole by gypsum and it is detected in both of them the presence of nitrates. In S sample there is a little absorption in the carbonates area as well as the presence of dolomite, no appearing in G sample. But W sample is completely similar to J sample except in the outer protecting coat which J sample lacks of it and its peculiarity of small wood pieces incorporation.

Through SEM/EDX the same results are corroborated. In the FIG. 4 it can be observed as an example a microphotograph of the old F mortar in which the gypsum and the calcium carbonate crystals are present.

Binder / Aggregate ratio: The mortar granulometric analysis allow to establish a relationship among their properties.

Their determination can be accomplished through a distribution curve of the size of particles or making a physical separation of each of the granulometric portions; in this way, it is possible to characterize them separately.

The upper and lower portions at 45 μm, expressing the proportion among binding material and aggregate, for J, O, S and W mortars are summarized in Table 2; for the rest it did not have enough sample and they are studied as a whole. The binder/aggregate ratio was found around 1:1. The S mortar could possibly be a later gypsum intervention, without aggregate. This ratio indicates a knowledge of the strength behaviour of the gypsum mortars (6) related to the lime mortars (7) in the past.

FIG. 4.- SEM Micrograph of J Mortar (P Group) (x3000)

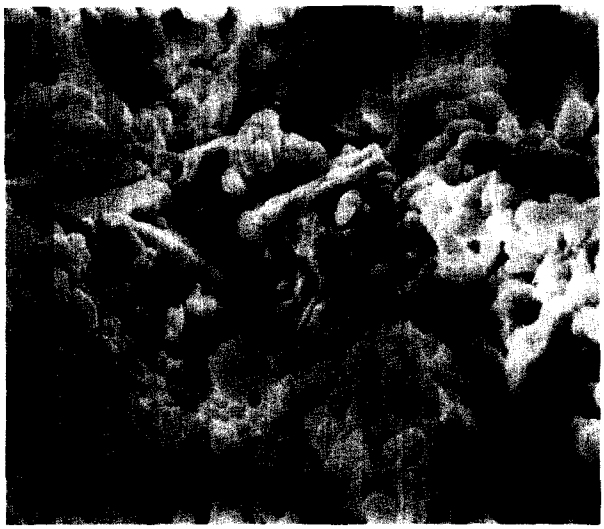

TABLE 2
Binder and Aggregate Percentage in Mortars

MORTAR (Reference)	FINE (%)	COARSE (%)
Group P - J	48	52
Group P - O	45	55
Group L - S	100	0
Group L - W	45	55

Aggregate characterization of mortars: The distribution curve of the size of aggregate particles of J and O mortars are presented in FIG. 5. The granulometry is in direct relation with the thickness of the corresponding joint. W mortar granulometry (FIG. 6) is similar to that of the J mortar; the wood particles, which weight for a same size aggregate is smaller, have been considered.

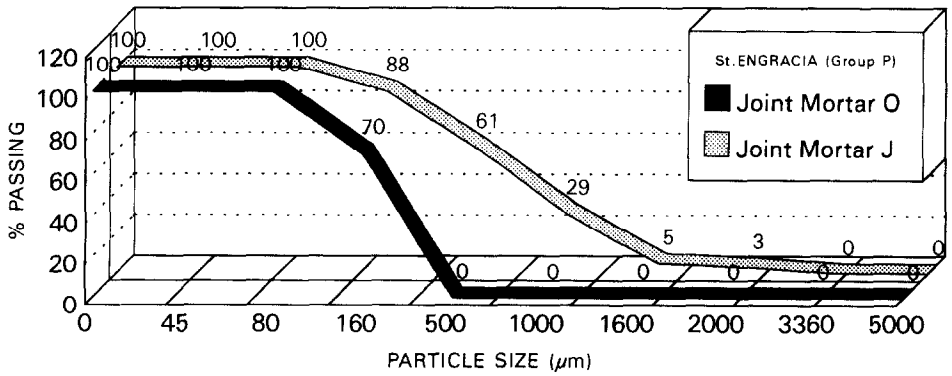

FIG. 5.- Granulometric Analysis of Aggregate Joint Mortars (P Group)

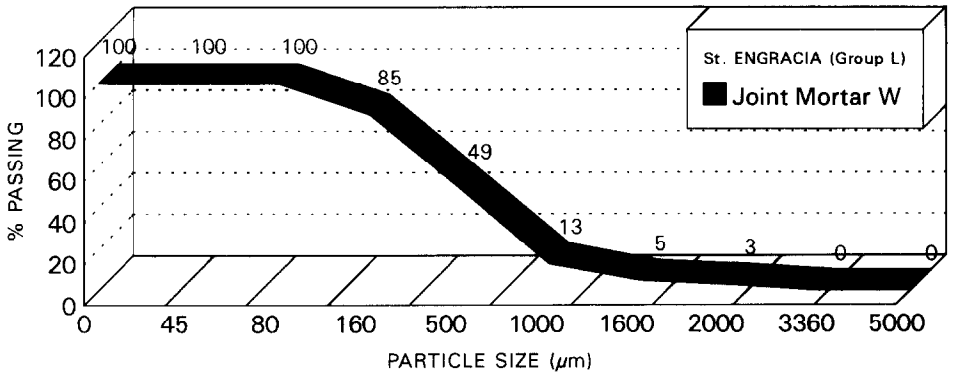

FIG. 6.- Granulometric Analysis of Aggregate W Joint Mortar (L Group)

The aggregate mortar characterization was accomplished through optical microscopy, XRD and SEM (FIG. 7). The optical microscopy allows us to appreciate the clayey particles in J aggregates. In W mortar not only the granulometry is very similar to that of J mortar but its physical appearance is alike too.

The mineralogical aggregate composition was studied through XRD. In J mortar aggregates (Group P) were identified gypsum, quartz, dolomite and calcite, similar to the aggregates of O mortar.

FIG. 7.- SEM Micrograph of J Mortar (x1000) (Aggregate "x": SiO_2)

Binder characterization of mortars: The study of binders is complementary to that for mortar samples in the whole described previously and, due to its lack of aggregates, coincides with S mortar (L Group). In the sample chemical analysis of J and O mortars from P Group it is included the percentage of SO_3 and the loss on ignition (LOI) (calcination residue at 950 $\pm$ 50 °C for 1 hour) which value expresses the loss of water of gypsum crystallization and carbonates content (Table 3).

The differential thermal analysis of the J sample offers two exothermal peaks corresponding to the water crystallization of gypsum (maximum around 120°C and 170°C) and an exothermal area with two maxima between 700 - 800°C due to the presence of carbonates.

The binder particle size distribution curves around 1 and 100 μm have been obtained with laser granulometer.

O and J samples have a similar fineness although J sample is a bit smaller. The maximum of distribution density curve corresponds to particles around 50 μm. In this curve they reflect more than a maximum, sign of the existence of a components mixture

within the binder of O mortar (FIG. 8).

The binder mineralogical composition was analyzed by IR spectroscopy and XRD.

The O and J binders IR spectra are similar to the corresponding mortars; they only present a bigger intensity in the carbonates and silicates absorption with regard to the sulfates. In O binder some nitrates could be detected.

TABLE 3
Chemical Characterization of the P Group Binders

Sample	SO_3 (%)	LOI (%)
J	41,0	11,4
O	31,8	14,8

The X-ray diffraction shows the existence of the following mineralogical compounds: gypsum ($CaSO_4.2H_2O$) main component, dolomite, and small proportion of calcite and quartz.

Mortar treatments: After the extraction treatment with chloroform-ethanol (8), and

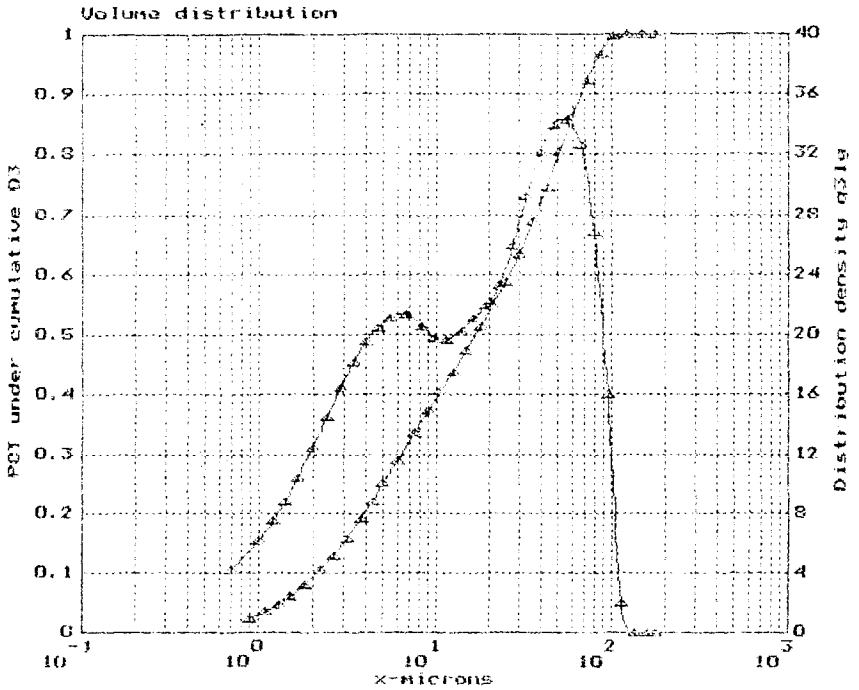

FIG. 8
Granulometric Analysis by Laser Ray Diffraction of the Binder of O Mortar

according to the their IR spectra interpretations, the binder mortar samples of the joint mortars can be classified as follows:

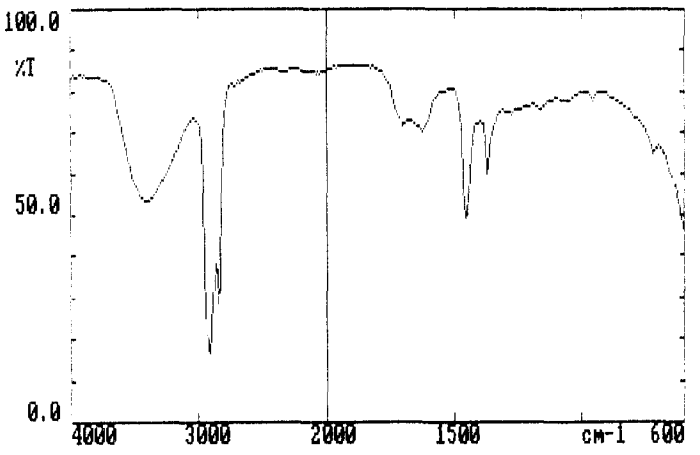

FIG. 9.- Mortar Treatments. IR Spectrum of the Extraction Residue of J Mortar

* Most commonly found are samples in which wax with drying oil in small quantity were applied: S, J, O, (FIG. 9).
* Some resin and possible wax with a small quantity of drying oil is detected in W sample.
* Sample G received a treatment based on egg yolk which reacted with calcium hydroxide.
* In F sample it is detected a treatment of drying oil reacting with calcium hydroxide and the present magnesium hydroxide.

REPAIRING MORTARS (R GROUP: K, L, P, T, X and Y samples):

K sample : This mortar was extracted from the right leg of Christ figure. It was gray color and inside it there were some white particles of small size. The adherence among the mortar and the alabaster was nonexistent in most of the joining area and consequently it was loose. At the moment of sample separation in granulometric pieces, it was observed the lack of coarse: 100% obtained were fine.

In the first identification through IR spectroscopy, it was detected that the sample was mostly constituted by calcium carbonate (calcite), gypsum, and absorption in the area of Si-O-Si (around 1000 cm^{-1}), apart from other organic compounds which were also present (FIG. 3).

The presence of Ca in almost all the sample as majority element was tested with SEM/EDX. The mineralogical composition was confirmed through XRD identifying calcite as majority compound, gypsum, quartz and amorphous material.

For the organic compounds detection it was used the extraction treatment with chloroform-ethanol and the residue was later analyzed by IR. It was also tested that the sample could probably corresponds to a resin mixed with wax and an addition of drying oil with the slaked lime of the middle part. This residue is similar to that of the T sample although this one has less resin.

L sample : This is a repair mortar sample of whitish color and tough shape. It was placed on the right ankle of Christ figure without any adherence to the alabaster. The sample was mostly constituted by gypsum according to the

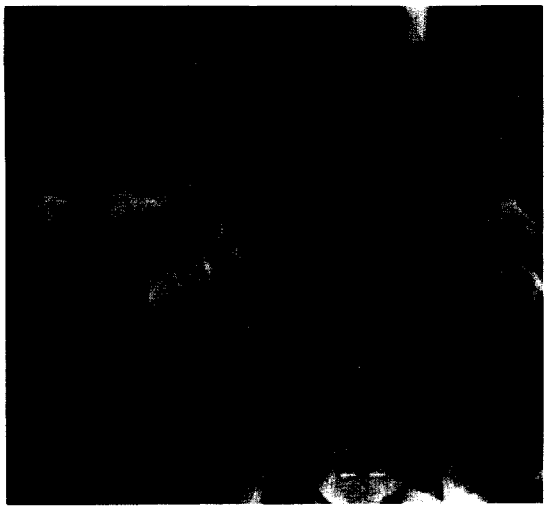

FIG. 10.- SEM Micrograph of L Repairing Mortar (x3600)

IR spectrum and it was possible to detect the presence of carbonates.

SEM/EDX allows to test its high composition of S and Ca and some small particles with Mg content (FIG. 10). The IR spectrum of extraction residue with chloroform-ethanol indicates a drying oil treatment with possible dryers, with a small addition of resin, and very reacted with lime (Ca and Mg). It is similar to F sample.

P sample : It was extracted from a repair made in St. Paula figure's sleeve (FIG. 1). It was whitish look and tough consistence. In its IR spectrum it is identified the high presence of gypsum.

The extraction chloroform-ethanol treatment indicates the presence of a fat very reacted with lime in the applied treatment.

T sample : T mortar was part of an alabaster piece re-engraving its original shape (FIG. 2). Its look is similar to that of S mortar. Its IR spectrum is constituted almost in the whole by gypsum with presence of nitrates.

After its extraction with chloroform-ethanol it can be deduced that the mortar probably contains colophony resin mixed with a small quantity of wax and drying oil.

X sample : It was extracted from the hollow of an old repaired anchorage coming from an alabaster piece which belonged to a fold from San Lamberto's figure. It was a whitish dust scarcely cohesive. Previous to the extraction treatment, the sample IR spectrum reveals the presence of gypsum and carbonates with a high content of organic compounds.

From the IR spectrum of the extraction residue treatment with chloroform-ethanol, it can be inferred the presence of mineral wax and drying oil reacted with lime in less quantity.

Y sample : It corresponds to the joining mortar of the above mentioned piece for its replacement. Its IR spectrum is practically the same to that of X sample. But with the IR spectrum of the extraction residue treatment with chloroform-ethanol, it can be inferred the presence of drying oil with dryers.

Conclusions

* In this paper there has been established a methodology of the study of the ancient mortars that includes the separation of the binder and the aggregates, dosage of binder/aggregate ratio, physical an mineralogical characterization of both, which also includes the detection of any additives with chloroform-ethanol and its posterior identification by infrared spectroscopy (8).

* The previous samples classification of P (ancient) and L (subsequent to the building and in some cases identified as belonging to Palao intervention) Groups, considered as an initial criterion in the study of samples can not be completely verified in the mortar characterization, due to the use of similar mortars based on gypsum mortars for alabaster at different epochs, although there exist some analogies among the components of each of the Groups.

* Mortars belonging to P Group (mentioned as ancient, extracted from inner joint areas) are constituted by the same kind of binder and aggregates with a binder/aggregate ratio of 1:1 suitable for gypsum mortars in opposition to the proportions of lime mortars (6, 7).

- Binders are mainly made up mainly by gypsum, with carbonates (dolomite with presence of calcite) and quartz; there are always organic compounds (wax with drying oil,...) and eventually nitrates. Their fineness are also similar.

- Aggregates also have a similar mineralogical composition: mainly gypsum, dolomite, calcite, quartz and argillaceous particles, but their granulometry is different depending on the mortar function in the monument.

The gypsum was a traditional building material in the past in many countries (9, 10) and specially in Spain. In this study is shown the ancient technique of adding lime, as well as clayey aggregates and other organic compounds to gypsum mortars.

* The studied mortars (S and G) from L Group (supposing that they come from Palao's intervention) also present a great similarity between them with regard to the binder.

- Most of them are gypsum mortars and only in some specific cases it is inferred the presence of carbonates.

- Aggregate is variable in its granulometry; nevertheless in most of the examples it was not verified its use; it was observed small gypsum agglomerates.

* Mortars from R Group (coming from restorations and repairs) correspond to specific samples of different interventions and the conclusions have been summarized in results and discussion with regard to each mortar separately.

As a general rule it can be said that they are mixtures of gypsum with variable quantities of carbonates, mixed with different kinds of organic compounds.

* The restoration mortars have been design with the support of these conclusions, according to the localization of the mortars and the compatibility criteria.

Acknowledgments

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