Characterization of ancient mortars: present methodology and future perspectives

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ABSTRACT:
This contribution is devoted to outlining our methodology for the study of ancient mortars and is the result of the collaboration between the University of Evora and the National Laboratory of Civil Engineering (LNEC) with leading Portuguese institutes, the Portuguese Institute of Architectural Heritage (IPPAR) and the Portuguese Institute of Conservation and Restoration (IPCR) aiming the development of integrated conservation strategies and the valorisation of the important architectural heritage of the South of Portugal (project CATHEDRAL - POCI/HEC/57915/2004).

1 INTRODUCTION

Mortars have been used in many applications (as renders, plasters, fillers, etc.) since remote times. Mortars are composite materials made of one or more types of binders, one or more types of aggregates, water, additives and with occasionally painted layers and are classified according to the type of binder used. Mortars based on lime technology prevailed since roman times until late XVIII century, when they became to be substituted by new hydraulic binders and finally by Portland cement, which completely displaced its use in civil and military constructions.
In the past, inadequate interventions in historic buildings, with systematic resource to modern solutions, were responsible for the disappearing of original renderings and finishings and have created new problems of functional incompatibility due to differences in mechanical and physical properties (strength, porosity, permeability, color) and chemical composition. The study of ancient renders, including mortars and paintings, and the characterization and mapping of degradation forms are of utmost importance to guarantee the conservation of ancient monuments and can give valuable information about their history and past interventions. Moreover, the design of new mortars, functional and aesthetic compatible, implies a detailed knowledge of the original mortars along with the definition of the functions to be performed by the new mortars.

2 METHODOLOGY

2.1 *Sampling*

The sampling of the mortars is a crucial step that can influence the success of the characterization methodology, as has been pointed out by several studies [1-3]. The size of each sample has to be carefully chosen to guarantee all the analyses and to allow confirmation or a "reserve" for future studies. The sampling is normally carried out using a hammer and a small chisel and the location is documented before and after removal of the sample. In-situ water absorption is often performed (RILEM test nº II.4 of RILEM commission 25-PEM) giving information about the water permeation kinetics which can be correlated with the capillary porous structure (pore size distribution) of the mortars obtained by mercury porosimetry.
In the laboratory, the first step is the thorough observation of the collected mortars using a stereo-zoom microscope to identify particular features such as lime lumps or additives (fibres, pozzolans, charcoal, etc.) and, if necessary, to separate different layers. The next step is the careful disaggregation of the samples, so as to avoid breaking the existing aggregates, to prepare samples for the several instrumental analyses that compose the mortars characterisation methodology.

2.2 *Microstructural and mineralogical analysis*

The mineralogical composition of the aggregates can be assessed by optical microscopy with data acquisition. Thin sections and polished surfaces are prepared by vacuum impregnation with low viscosity epoxy resin and observed under transmitted or reflected polarised light, enabling the identification of the morphology, dimension and type of aggregates, binder, additives, apparent porosity and cracking and secondary or decay products. This analysis can also give information on the spatial interrelationships of mortars components and aggregate/binder interfacial reactions (see figure 1).

The petrographic observations are compared and correlated with the X-ray diffraction analysis (XRD) performed on a Phillips X'Pert diffractometer and a Bruker AXS D8 Advanced diffractometer. Two types of fractions are analysed by XRD, the fraction corresponding to the mortar as collected, designated as *overall fraction* and obtained by grinding the disaggregated mortar to pass in a 106 µm sieve and the other fraction, designated as *fine fraction*, which has a higher binder concentration and is obtained from the fines of the disaggregated material passing by a 106 µm sieve. XRD is used not only to complement the identification of the crystalline phases of the mortars components but also to identify pozzolanic reaction materials as well as alteration/damaging products, like salts. However, it cannot detect minor crystalline phases (detection limit is approx. 3%) and does not provide information on the spatial distribution of the mortars components (bulk technique).

Scanning electron microscopy observations, performed on a scanning electron microscope (SEM) JEOL JSM-6400 coupled with a OXFORD energy dispersive x-ray spectrometer (EDX), allow a further insight on the mortars composition and morphology. Particularly, it can be used to examine the binder morphology, the textural interrelationships of the components and phases present that are too small to observe by optical microscopy, like salts, pozzolanic products or organic/biological microorganisms (see figure 1). The EDX spectra allow the elemental analysis of the mortars components, and hence, complement the XRD analysis. Prior to analysis, the samples are coated with a thin film of carbon or gold in a vacuum evaporation system.

Ultimately, the mineralogical composition of the mortar components is compared with the geological charts and available historical documentation, allowing, in some cases, the identification or confirmation of the provenance of the original raw materials, particularly aggregates and binder.

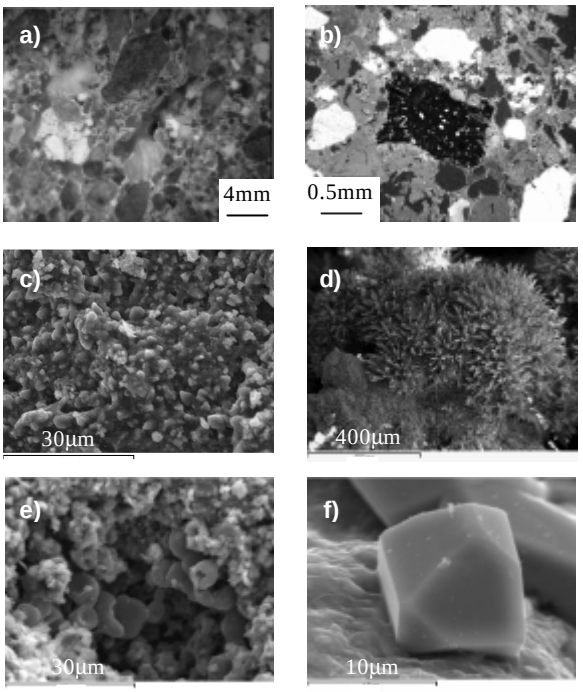

Figure 1. Detail of a) a polished section and of a b) thin-section of the mortars showing crushed ceramics, lime nodules and siliceous sand; SEM micrographs of c) microstructure of a lime matrix d) hydrated calcium silicate crystals growing at the surface of an aggregate, e) biological colonization and f) halite crystal.

2.3 *Chemical analysis and mortar composition*

Chemical analysis by wet digestion is a common technique used to determine the approximate binder/aggregate ratio.

For the chemical analysis of the binder components, a small portion of the mortar is carefully disaggregated and all types of impurities and limestone grains are separated. Chemical analysis is performed after partial digestion of the mortars with warm diluted hydrochloric acid (1:3) to separate the siliceous aggregates from the lime paste. For the soluble fraction, the amounts of calcium, magnesium, aluminium, iron and sodium (expressed in terms of their oxides) are determined by atomic absorption spectrometry, chlorine ion is determined by potentiometry while sulphate ion is determined by gravimetry. These results can be used to identify the hydraulic and non-hydraulic properties of traditional mortars and the presence of soluble salts and alkalis which are important to evaluate the degradation of the mortars [4]. The results are correlated with those from the mineralogical analysis.

The insoluble residue is weighed and sieved to determine the particle size distribution of the aggregate fraction i.e. the siliceous sand. However, this method is limited to mortars with siliceous sand because calcareous aggregates dissolve during the acid attack.
The mortar's binder composition and CO_2 content is assessed by thermogravimetry (TGA) and differential thermal analysis (DTA) performed on a SETARAM TGA-DTA analyser, under argon atmosphere, with heating rate of 10°C/min, from room temperature to 1000°C. TGA measures the weight (mass) change of a sample as a function of temperature while the DTA measures the energy changes, represented by endothermic or exothermic peaks in the DTA curve. Quantitative analysis is based on the TGA curves (thermograms) while DTA provides information for the qualitative identification of the components that undergo weight losses [1,3].
The simplified compositions of the mortars can be estimated on the basis of the method designated as "Jedrzejewska" [5] referring to old lime mortars combining the calcium carbonate % estimated by TG/DTA with the residue analysis. This method considers three type of components: "carbonates", acid "soluble fraction" (compounds soluble in acid without formation of carbon dioxide) and "aggregates" (corresponding to insoluble residue of the acid attack).

2.4 *Physical analysis*

Physical and mechanical characterisations are important requirements for the development of compatible mortars. However, for ancient mortars they are sometimes impossible to evaluate due to the difficulty to do rigorous determinations with irregular, friable specimens, cutting standard-sized test samples or sampling from an ancient wall of high aesthetic value. The tests that are most often performed are compressive resistance, water absorption and porosity.
For the compressive resistance test, a cubic sample is required. The samples are placed in a press and the compressive force is increased until breakage of the sample. Prior to this test, the standard-sized samples are used to determine the water absorption coefficient. This method consists in measuring the water adsorbed as a function of time by a standard sized sample in contact with a water surface. By plotting the water adsorbed (in mass per unit area) as a function of the square root of time it is possible to obtain an initial linear region whose slope corresponds to the water absorption coefficient and hence is a measure of the water permeability. All samples are dried at 60ºC during 24 hours.
The porosity is assessed by nitrogen adsorption and mercury porosimetry which allow the determination of several structural parameters namely pore volume, specific surface area and pore size distribution. The results obtained by these two techniques are complementary and enable a full and detailed characterisation of the porous structure of the mortars varying from macropores to micropores. These methods have the advantage of requiring very small samples. The results obtained are compared and correlated with those obtained by mineralogical and chemical characterization showing the importance of mortar composition and porous structure in the deterioration of masonry monuments and buildings.

2.5 *Chromatic layer analysis*

Whenever painted layers exist, it is important to identify and characterize its constituents and features like, for example, the number and thickness of each layer, the type of pigments and their proportion. The first step is the preparation of polished cross-sections by impregnating the sample (which in the case of mural paintings is in the order of a 1-2 mm^2) with an epoxy resin and cutting it perpendicularly to the layer. Optical observation (see figure 2a) of cross-sections enables the study of its layered structure together with the measurement of the thickness of each layer of paint, color, texture and pigment particle size [6]. These observations are followed by microchemical identification of the pigments and binders using the method developed by Plesters [7]. This method is a modification of the classic inorganic qualitative analytical procedure for samples with very low dimensions and for the detection of specific cations and anions that allow identification of particular pigments. Afterwards, the cross-sections are prepared to be analysed by SEM-EDX which allows not only the elemental analysis of the pigments and binders (using the EDX), and ultimately their identification (see figure 2), but also the mapping and study of the pigments morphology.
In the study of mural paintings, two other techniques are available and seldom used, micro-XRD performed on a Bruker AXS D8 discover diffractometer and *in-situ* X-ray fluorescence spectrometry (XRF) performed on a EIS SRL XRS 38 spectrometer.
The former is normally used for the confirmation of a specific pigment (for example, elemental analysis may detect a specific element but may be insufficient to distinguish pigments).

The latter is used in the study of mural paintings whenever sampling is not an option. *In-situ* XRF has the advantage of being non-destructive, multi-elemental, fast and cost-effective. XRF can analyze inorganic pigments, but cannot obtain information about organic dyes, because it is not sensitive to lighter elements (lower than potassium). XRF analyzes a small point, of approximately 5mm diameter, and is based in the fact that the incident X-rays interact with the electrons of an atom in a pigment particle generating a spectrum which is specific to the pigment analyzed.

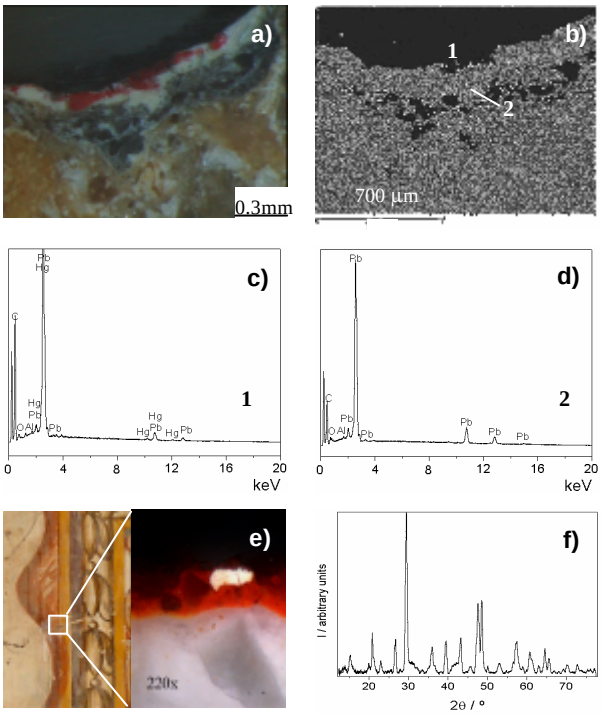

Figure 2. a-d) Cross-section of a mural painting from the *Freixo de Espada-à-Cinta Church*: a) optical micrograph b) SEM micrograph, c) EDX spectrum of the red layer, showing that the pigment is vermillion (presence of Hg) c) EDX spectrum of the white layer, showing that the pigment is white lead (presence of Pb); e-f) Cross section of a mural painting from the *St. António dos Capuchos Covent* in Estremoz: e) detail of the painting and optical micrograph of a cross-section and d) XRD pattern of the red pigment (typical of an ochre).

3 FINAL REMARKS

A mortar is a complex mixture of aggregates (sand grains), binder and water. The analytical methodologies used vary according to the information required and the aim of the study and focus on a specific detail or characteristic of the buildings materials.

The chemical and mineralogical study of ancient mortars may give information about binder and aggregates composition, neo-formation compounds and decay products, pigments and additives and may corroborate or question historical research or the mortars present knowledge. However, it lacks information about the physical properties of the mortars like mechanical resistance, permeability and porosity which can be assessed by other techniques such as compression testing, water sorption, mercury porosimetry and nitrogen adsorption. The present methodology is a rational combination of the two approaches and allows settling down with enough precision the "whole picture" giving essential information for the planning of the conservation intervention and the formulation of compatible repair materials. It is worth mention that, recent technical developments are improving the capacities of material characterization, including cultural heritage materials. Especially rewarding is the increased availability of 3rd generation Synchrotron Sources. These facilities optimized the conditions to sustain microbeam techniques as Micro-XRD, Micro-FTIR, Micro-XAS, Micro-XRF and X-ray Microtomography. Spatially resolving techniques as that are especially welcome when the main goal is the characterization of so heterogeneous materials as mortars.

4 REFERENCES

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