

Characterisation of roman mortars from the archaeological site of Tróia (Portugal)

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Abstract

Roman mortars from the industrial archaeological site of Tróia (Portugal) have been studied by means of chemical, mineralogical and microstructural analysis. The mortars are calcitic aerial lime mortars differing in the type and proportion of aggregates used, including crushed carbonaceous rocks (limestone and dolomite), siliceous sand and crushed ceramics. The results show that although these mortars have been subjected to a very aggressive environment they are still in a very good state of conservation.

Introduction

Tróia's peninsula (Grândola, Portugal) presents one of the most important roman sites known in Portugal, declared as National Monument since 1910. Built by the end of the I.B.C. or beginning of I A.D., along river Sado's Estuary, facing Setúbal harbour city and ranging almost 2 km in extension, the site comprises a considerable dense set of constructions, including fish salting industries, houses, baths, cemeteries and a religious temple (fig. 1).

The main purpose for this settlement is clearly connected to the industrial processing of sea products. In fact, this is one of the largest complexes from the Roman Empire known, revealing a great economical significance of fish conservation and trading activities.

This industry achieved great activity until the middle of III AD. By that time it began a progressive and irreversible decadence process until the fifth century.

Those factories are composed of organised sets of fish-salting reservoirs (*cetariae*) divided by masonry walls. Each unit included a central pavement area and in their vicinity were found wells for the collection of water. The fish were washed and prepared for salting inside the *cetariae*. Herbs and spices were mixed with fish viscera and submitted to maceration and fermentation process to obtain sauces. The roman most famous product was fish based sauces like *garum*. These final products were bottled in amphorae and were exported towards several parts of the roman world.

The aim of this work is to obtain structural information about the roman mortars from Tróia useful for the prevention of decay mechanisms and for the formulation of appropriate compatible repair mortars.

Sampling methodology

Mortar samples were collected from the pavement of *cetariae* located close to the sea river (fig. 1). Drilling of pavements showed the existence of a clay layer that served as basis for the foundation mortar. The collected samples were two foundation mortars (TPh31 and TPh34) and one covering mortar (TPh33).

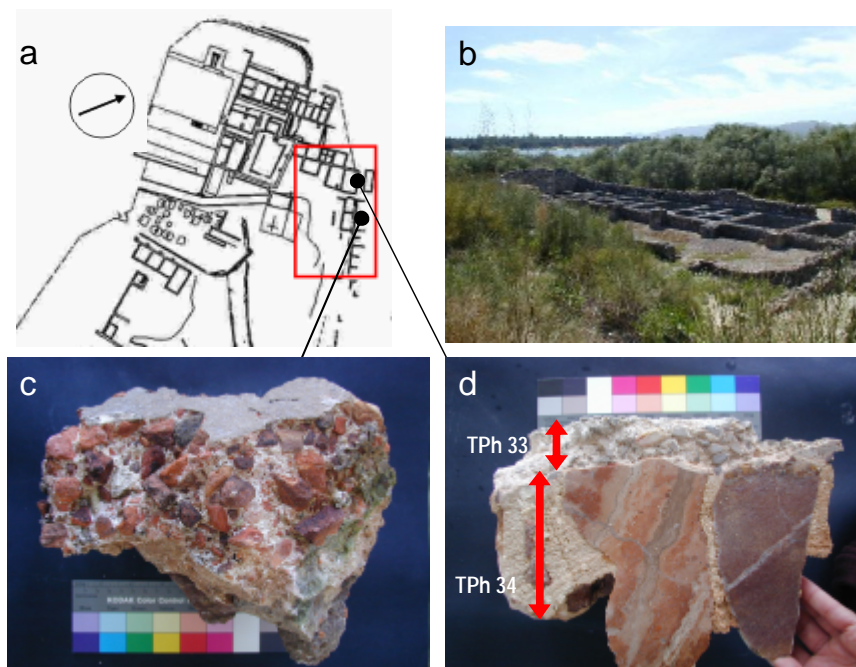


Fig. 1 a) Plan and b) partial view of the industrial nucleus of the Archaeological site of Tróia. c) Detail of foundation mortar TPh31 and d) cross-section showing covering mortar TPh33 and foundation mortar TPh34.

Characterisation methodology

The mortars were thoroughly observed in laboratory in the naked eye and using an Olympus stereo-zoom microscope and disaggregated with care so as to avoid breaking the existing aggregates. During disaggregation, it was observed that mortar TPh31 was much more resistant than mortars TPh33 and TPh34.

The microstructure of the samples was observed on a scanning electron microscope (SEM) JEOL JSM-6400 coupled with a NORAN electron probe microanalyser (EDS).

The mineralogical composition was evaluated by X-ray diffraction (XRD) using a Phillips diffractometer with Co $K\alpha$ radiation. Two types of fractions were analysed, the fraction corresponding to the mortar as such, designated as *overall fraction* and obtained by grinding the disaggregated mortar, so that all particles assume a sufficient size to pass in a 106 μm sieve and the other fraction, designated as *fine fraction*, which has a higher binder concentration and was obtained from the fines of the disaggregated material passing a 106 μm sieve. The *overall fraction* of each sample was also used for thermal analysis (TG-DTA) performed in a SETARAM TG-DTA analyser, under argon atmosphere, with heating rate of 10 $^{\circ}\text{C}/\text{min}$, from room temperature to 1000 $^{\circ}\text{C}$.

For the chemical analysis, mortars were carefully disaggregated and all types of impurities and limestone grains were separated. Samples were afterwards attacked with warm diluted hydrochloric acid (1:3) to separate the fraction corresponding to siliceous aggregates.

All mortar samples, after being prepared, were dried at 40 °C for at least 12 hours, with exception of the samples for chemical analysis, which were dried at 105 °C.

Results and discussion

Optical microscopy observations showed the presence of siliceous sand with rolled morphology and sizes lower than 5 mm in all samples. Stone aggregates with sizes larger than 5 mm were present in samples TPh31 and TPh33. Sample TPh31 showed also a large amount of red and black brick fragments with sizes greater than 5 mm and the paste evidenced the presence of brick powder.

The mineralogical composition of the mortars by means of XRD is summarised in table 1.

Table 1. Qualitative mineralogical composition of mortar samples

| identified crystalline compounds | TPh31 | | TPh33 | | TPh34 | |
|----------------------------------|----------|---------------|---------|---------------|---------|---------------|
| | overall | fine fraction | overall | fine fraction | overall | fine fraction |
| quartz | +++ | + / ++ | + | + | +++ | ++ / +++ |
| feldspars | + | vtg | vtg | - | + / ++ | vtg |
| mica | vtg / + | vtg | - | - | - | - |
| hematite | vtg | vtg | - | - | - | - |
| calcite | ++ / +++ | +++ | +++ | +++ | + / ++ | +++ |
| aragonite | - | - | vtg / + | + / ++ | - | - |
| vaterite | - | vtg | - | - | - | - |
| dolomite | - | - | +++ | + | - | - |
| hydrated calcium chloroaluminate | vtg | vtg / + | - | - | - | - |
| halite | - | - | vtg / + | + | vtg / + | + |

++++ very abundant; +++ abundant; ++ present; + small amount; vtg traces; - undetected

The results are characteristic of aerial lime mortars prepared with siliceous sand, possibly from the sea river due to their rolled morphology and very low concentration of mica and feldspar.

For sample TPh31, separate analysis of the different types of aggregates, namely red and black bricks and grey stones was also performed. The results showed that the composition of the bricks is quite identical. However, the presence of mullite in the red bricks and the absence of clay minerals show the use of a higher temperature in the baking of these materials. The grey stones present were found to be of a dolomitic nature. The presence of hydrated calcium chloroaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) compound in this sample, other than indicating the action of a chloride-ion rich environment, such as seawater, it represents the formation of compounds of a hydraulic character, as a result of the integration of materials with “pozzolanic” characteristics, namely the *redder bricks*. This so called “pozzolanic” character of the crushed bricks is attributed to the alkali-silicate reactions occurring at the ceramic-matrix interface; their nature depends both on the type of ceramic and the calcium hydroxide content of the mortar [1].

The results for sample TPh33 show that this aerial lime mortar was prepared with crushed stones of a dolomitic and calcitic nature as well as of sand of a siliceous nature. The presence

of aragonite and halite is related to the action of seawater. Sample TPh34 showed a lower content of calcite in comparison with the others. Like the other mortars, this sample is contaminated by chlorides (halite).

The grain size distribution of the sand present in the mortars (fig .2) was determined by sieving of the residue obtained from hydrochloric acid attack. Since sample TPh33 proved to be very rich in limestone aggregates, a different test protocol was used so as to determine the approximate proportion of limestone aggregates present in the sample. In this case, the attack time of samples was shorter and with cold 14% hydrochloric acid solution.

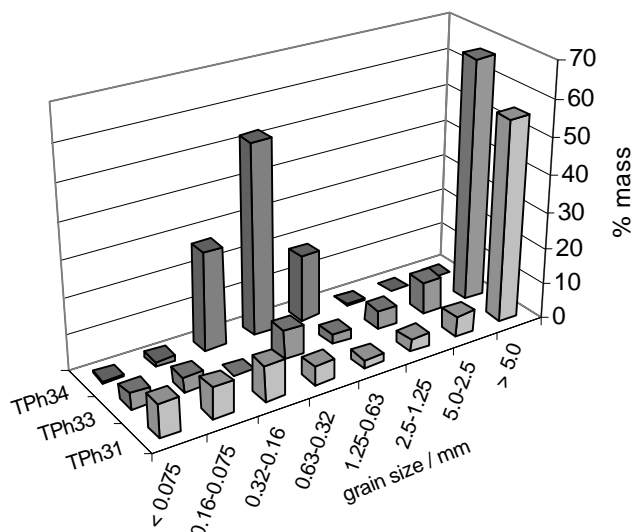


Fig 3. Grain size distributions of residues of the analysed mortars (values in %).

The results show a significant dispersion in the aggregate sizes, mainly due to the high variability in the type of aggregates used. In fact, most aggregates in sample TPh31 have sizes larger than 5mm and correspond to ceramic fragments, and most aggregates in sample TPh33 have sizes also larger than 5mm but have a calcareous origin, whereas aggregates in sample TPh34 are fine (< 0.630 mm) and have a siliceous nature.

The determination of the simplified composition of the three mortars (table 2) calculated on the basis of the method designated as "Jedrzejewska" [2] referring to old lime mortars was made possible by combining the weight losses results obtained from TG-DTA with the residue analysis. This method considers three types of components: "carbonates", acid "soluble fraction" (compounds soluble in acid without formation of carbon dioxide) and "sand" (corresponding to the insoluble residue of the acid attack).

Table 2. Simplified composition of mortar samples (mass %).

| samples | components | | | | | |
|---------|-----------------------|-------------------------------|---|-----------------------------|-----------------------------|-----------------------------------|
| | "sand" ⁽¹⁾ | "sand + brick" ⁽¹⁾ | "sand + aggregate limestone" ⁽²⁾ | "carbonates" ⁽³⁾ | "carbonates" ⁽⁴⁾ | "soluble fraction" ⁽⁵⁾ |
| TPh31 | - | 61 | - | 27 | - | 12 |
| TPh33 | 6 | - | 75 | 57 | 28 | 9 |
| TPh34 | 77 | - | - | 22 | - | 1 |

⁽¹⁾ Residue in HCl (1:3); ⁽²⁾ Residue in HCl (14%); ⁽³⁾ Represented in CaCO₃, calculated from the CO₂ content determined by TG; ⁽⁴⁾ Represented in CaMg(CO₃)₂, calculated from the CO₂ content determined by TG; ⁽⁵⁾ Fraction soluble in HCl = 100 - Σ(IR + Carbonates).

Scanning electron micrographs are shown in Fig 3. The observations showed that sample TPh31 has a compact microstructure rich in gels of the type of the ones formed in hydraulic binder mortars whereas samples TPh33 and TPh34 show a typical microstructure of a lime mortar composed of tiny calcium carbonate crystals [3]. The presence of aragonite in the cracks and pores of the “paste” of all the samples can be justified by a carbonate dissolution-recrystallization process of the binder. The halite crystals observed are due to the presence of nearby seawater.

The surface of the grains of the quartzitic sand present in sample TPh31 have a rounded morphology and are usually “attacked”, which explains the value of the soluble fraction obtained (Table 2). Indeed this soluble fraction indicates the higher or lesser formation of compounds of a pozzolanic character between the aggregate minerals and lime.

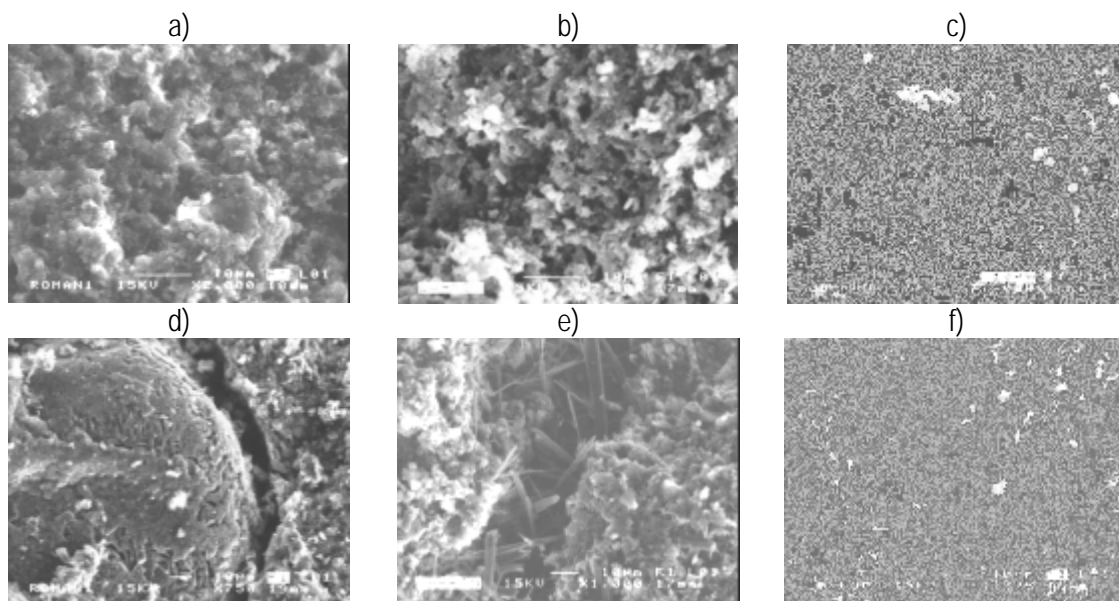


Fig. 3. General aspect of the microstructure of the lime “paste” of sample a) TPh31 , b) TPh33 and c) TPh34; and microstructure of d) quartz grain, e) microfissure of the paste filled with aragonite crystals and f) halite crystals.

Final considerations

The studied samples are calcitic aerial lime mortars that differ among them with regard to the proportions and types of aggregates used. Mortar TPh31 showed better mechanical properties possible due to an important content of hydraulic compounds in the lime paste which is related to the inclusion of crushed fragments and fine particles of ceramics materials. The current weight composition of each mortar estimated using the results from table 2 are:

TPh31 – 18% hydrated lime: 61% siliceous sand and brick : 2% crushed dolomite

TPh33 - 12% hydrated lime : 6% siliceous sand : 41% crushed limestone : 28% crushed dolomite

TPh34 - 16% hydrated lime: 77% siliceous sand.

References

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