Characterisation of mortars from Tróia Archaeological Site

Esteves, A. M.
Chemical Engineer/ Senior Research Officer, Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, aesteves@lnec.pt

Catarino, J.
Chemical Engineer/ Trainee, Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, jcardoso@lnec.pt

Delgado Rodrigues, J.
Geologist / Principal Research Officer (ret.), Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, delgado@lnec.pt

SUMMARY: Summary up to 300 words maximum

This paper presents results obtained in the European project PRODOMEA (PROject on high compatibility technologies and systems for conservation and DOcumentation of masonry works in archaeological sites in the MEditerranean Area). The aim of the project was to create a new approach for assessment of the compatibility of conservation treatments on masonry architectural assets and elements present in Roman age archaeological sites in the Mediterranean Basin.

This paper presents the characterization procedure applied to the Roman mortars employed in the archaeological site of Tróia, Portugal, one of the project case-studies. The characterization procedure and results are presented and discussed.

KEY-WORDS: Binder characterization, Roman mortar, Tróia archaeological site

INTRODUCTION

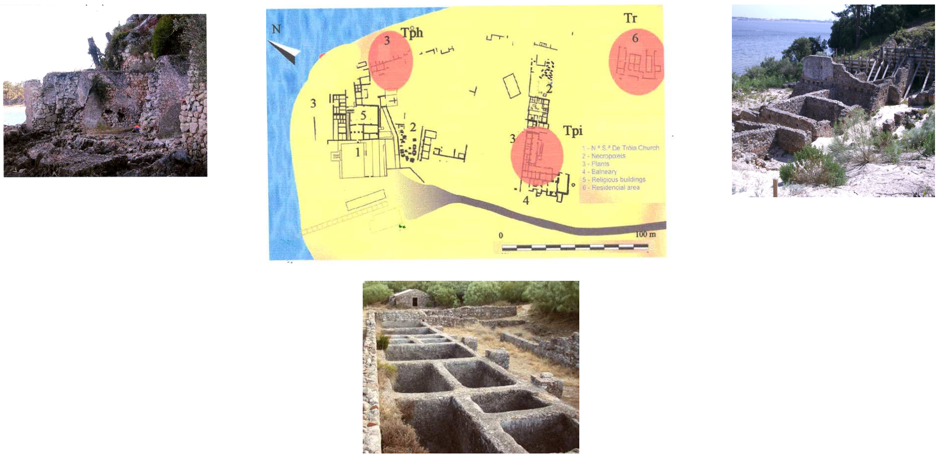
It is generally considered that most conservation interventions, even in archaeological sites, carry a certain level of risk and that it is neither technically nor economically feasible to advise that only interventions without risk should be acceptable. Therefore, the ultimate achievable aim is certainly not to find "perfectly compatible" actions, but to find those that minimise the degree of incompatibility. The European project PRODOMEA (PROject on high compatibility technologies and systems for conservation and DOcumentation of masonry works in archaeological sites in the MEditerranean Area) considered to focus in the search for a better understanding of the real meaning of *compatibility / incompatibility* (1) and therefore the sampling and testing on the sites aimed at contributing to improve the conservation strategies used on archaeological masonry, namely by searching for a more compatible, structured and sustainable one.

The partners in charge of the collection of samples conducted their campaigns on the five archaeological sites studied under this project: Troia (Portugal), Giannutri (Italy), Damascus (Syria), the Mekawer Fortress and Petra (Jordan)[(2)]. To fulfil this objective the team started collecting the available technical data relating to material characterisation of each site and to previous conservation treatments, followed by individual sampling campaigns in the five project sites[(3)]. A sampling campaign was carried out in Tróia, Portugal, where several samples were collected [(2)].
Tróia is located in the peninsula with the same name, in the Atlantic coast of Portugal, and comprehends a fish processing industrial complex with a considerable dense set of buildings including plants, residential area, Roman baths, funerary structures and a religious temple[(4)]. The fish-salting industry of Tróia was part of a complex trading chain centred in the Mediterranean Sea that guaranteed the supply of sea products to a significant set of the Roman Imperial population centres.
Since mortars are complex systems, different approaches can be used for their characterization, as widely reported in the literature[(5)]. Actually the reconstruction of the original composition is quite complex and requires the application of various and complementary techniques.
The characterization of historic mortars is of main concern in the field of Cultural Heritage in order to evaluate the technologies of construction, the conservation state of materials and to plan appropriate conservation actions. Investigation of binder and aggregate composition has an historical value as it may indicate the provenance of raw materials and increase the knowledge of the technology level of a specific historic period. From the conservation point of view, the binder aggregate ratio is of high interest, as it can guide on the definition of conservation works.
In this paper the characterization procedure and results of four mortars collected at the archaeological site of Tróia are presented where the aggregates, the binder and the binder aggregate ratios were identified. Bedding mortars collected at a damage brick wall for soluble salts analysis and a core sample to enhance the construction technology were also studied.

SAMPLES

The mortar samples were collected on the basis of their chronology, typology of construction and location as regards the proximity to the nearest shoreline. Therefore samples of mortars from Roman masonry were collected in the residential area (Tr), in the interior fish plant (Tpi) and in the fish plant at the harbour area (Tph). The Tróia archaeological site plan and the location of sampling are presented in Figure 1.
In this paper the results of the samples, 2, 5 and 20 inform about aggregates and binder characterization, as well as on the construction technology at the site. Samples 10, 11, 12, 13 and 14 were collected for soluble salts determination along a vertical profile of the wall at the residential area with the objective of identifying possible phenomena of raising damp.
Mortar sample 2 collected at Tpi was a plaster finishing layer from a fishing salting tank (*cetariae*). This mortar presented good cohesion and was quite hard. Some biological colonisation was observed on the exposed surface (Figure 2).

Tph Tr



Tpi

Figure 1.Plan of Troia archaeological site and of the sampling areas: processing plant at harbour (Tph), processing plant at interior (Tpi) and residential area (Tr)

Figure 2. Sample 2 and fraction of 1.25mm of quartz aggregate.

Mortar sample 5 collected at Tpi was a plaster preparatory layer collected in a *cetariae*. In the late Roman period this *cetariae*. was subdivided in three parts. The plaster preparatory layer belongs to a second layer of a bedding mortar and has aggregates with different composition, sizes and shapes, where limestone aggregates prevail (Figure 3).

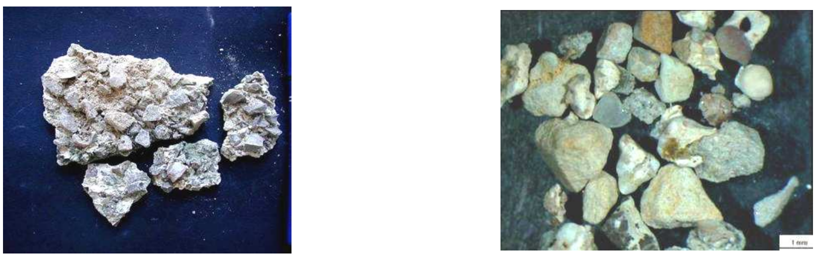


Figure 3- Sample 5 and fraction of 5mm of lime aggregate.

Mortar sample 20 collected at Tph was a plaster preparatory layer from the bottom of a *cetariae*, representing a typical *cocciopesto* mortar in texture and composition and has high cohesion. This sample contained brick fragments, well sorted limestone and quartz aggregate and an incipient biological colonisation on its exposed surface (Figure 4).


Figure 4. Sample 20 and fraction of 5mm aggregate with brick and quartz particles.

Sample 36 was a core collected at the bottom of a *cetariae* at Tpi (Figure 5) and is representative of the type of Roman construction technology. It was constituted of a bottom layer of clay followed by upper layers with different sizes of aggregate from coarser to finer ones. It suggests that this clay layer might have been used to give waterproof conditions to the *cetariae*.

Figure 5. Aspect of sample 36

CHARACTERIZATION PROCEDURE

In order to characterise the samples a systematic protocol was followed where colour, texture, aggregate morphology, aggregate sorting and the function of the mortar (plaster, render, structural, decorative, etc) were recorded. The procedure applied for characterization the mortar samples to determine the binder/agregate ratio and the soluble salts content is presented in the flow chart below (Figure 6).

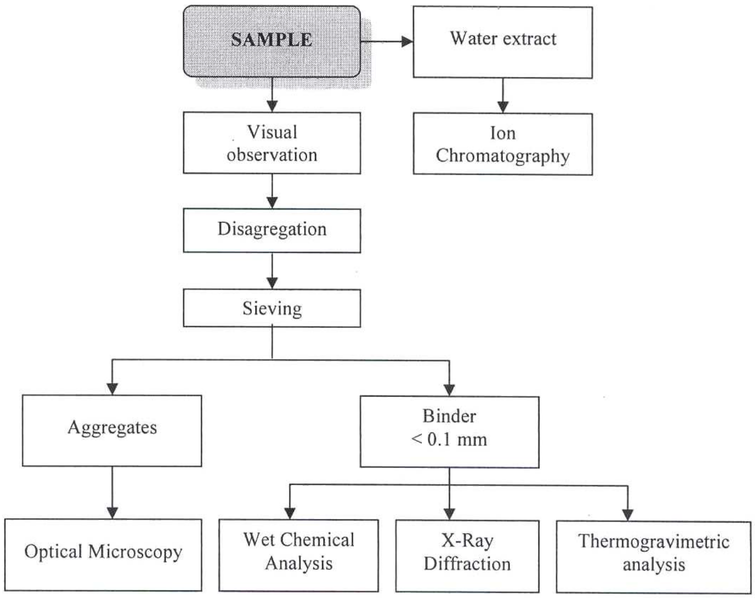


Figure 6. Flowchart of Roman mortar characterization

RESULTS AND DISCUSSION

Binder and aggregates characterization

Aggregates were separated from the binder by manual disaggregation using a small hammer with high care so as to avoid excessive breaking of the aggregates. After disaggregation, the sample was sieved using the following meshes: 16mm, 8mm, 5mm, 2.5mm, 1.25mm, 0.630 mm, 0.315 mm and 0.106 mm. The fractions retained on sieves 0.630, 0.315 and 0.106 mm were smoothly ground together in an agate mortar and passed in the 0.106mm mesh sieve. The fraction that still remains on sieve 0.106 mm corresponds only to siliceous sand as observed by optical microscopy. After separation of the fractions the siliceous aggregates were washed with diluted nitric acid and the calcareous aggregates washed with water and observed by optical microscopy.

Aggregates were identified by optical microscopy as quartz in sample 2, limestone and quartz in sample 5 and quartz mixed with brick in sample 20. The binder/aggregate ratio was determined considering the weight of the respective fractions.

The chemical characterisation of the binder was carried out on the fraction <0.1mm by wet chemical methods using hydrochloric acid (1:1) to dissolve the binder. Calcium and magnesium in the acidic solution were determined by complexometry with EDTA and silicon by spectrofotometry with ammonium molibdate. Carbon dioxide was determined in the solid sample through the difference between the mass loss at 450ºC and at 850ºC.

Calcium carbonate was estimated considering the results of calcium and carbon dioxide obtained (Table 1).

Table 1.Chemical composition of the binder fraction.

Sample	**CaO %**	**MgO %**	**SiO_2 %**	**CO_2 %**	**$CaCO_3$ %**
2	13.3	0.9	0.6	11.2	25.5
5	41.8	5.0	0.4	31.0	70.5
20	18.5	1.7	0.9	13.8	31.4

From the results on Table 2 it can be seen that lime content of the samples expressed as calcium carbonate varies between 25.5% and 70.5%. The X-ray diffraction analysis was used on the binder fraction of the samples to confirm the mineralogical compounds; the respective diffraction patterns are presented in figure 9.

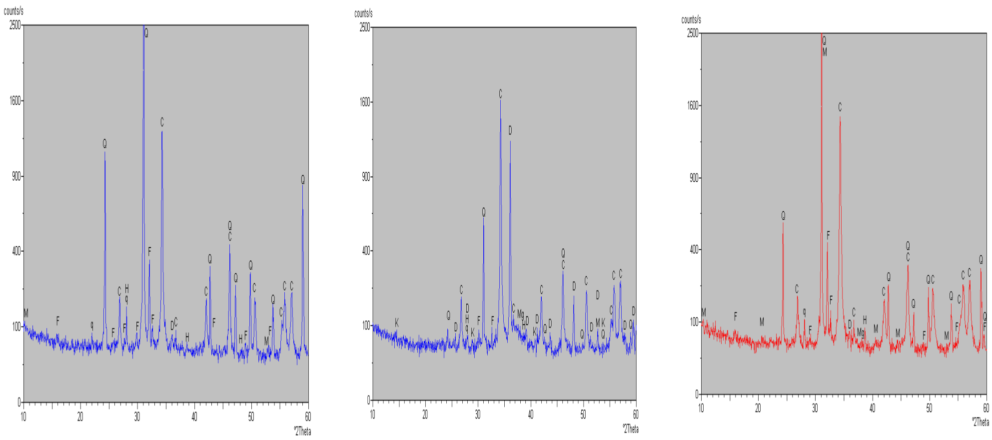


Figure 7. X-ray diffraction patterns of samples 2, 5 and 20 (from left to right)

The semi-quantitative results of the X-ray diffraction analyses is present in Table 2 and using the notation below it is possible to have an approximate relative proportion of the different crystalline compounds identified.

++++ very high	+ very low
+++ high	? doubtful
++ medium	- undetected

Table 2. Mineralogical composition of binder fraction

Crystalline compounds	Sample 2	Sample 5	Sample 20
Quartz	+++	+/++	+++
Feldspars	+	traces	+
Mica	?	-	traces/+
Calcite	+/++	++	+/++
Dolomite	traces	+/++	traces

Quartz is the main constituent, 2 and 20 being the richest samples. The detected feldspars and mica are components usually found in siliceous aggregates as contaminants of siliceous aggregates. Dolomite is present in sample 5 in agreement with the higher content of magnesium determined in this sample (Table 4). All samples contain calcite as a predominant component. By means of thermogravimetric and differential thermogravimetric curves (TG/DTG) of samples 2, 5 and 20 the thermal decomposition of the binders was recorded (Figure 8).

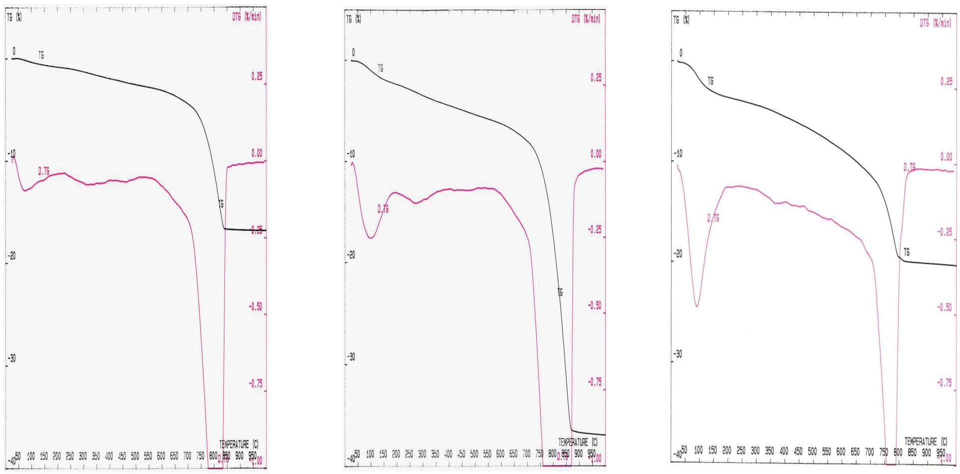


Figure 8. TG and DTG curves of sample 2, 5 and 20 (from left to right)

By comparing the thermogravimetric curves of these samples we could confirm that the binder contains mainly carbonated lime, with sample 5 showing the highest $CaCO_3$content..
Table 3 presents the results on the percentage of aggregates by size, the type of aggregate and binder and the binder/aggregate ratio (B/A).

Table 3. Aggregates by size and type, binder type and binder/aggregate ratio (B/A)

Sample	Aggregate size and percentage in weight					Binder Type	B/A
	0.106mm	1.25mm	2.5mm	5mm	8mm		
2	Quartz 47%	Quartz 8%	0	0	0	Lime	1:1
5	Quartz 6%	Quartz 11%	Limestone 19%	Limestone 20%	Limestone 34%	Lime	1:9
20	Quartz Brick 13%	0	Quartz Brick 9%	Quartz Brick 38%	0	Lime Brick	1:1

Mortars contained quartz limestone and brick as aggregates and the binder was calcitic lime and calcitic lime with brick. The binder aggregate ratio for samples 2 and 20 was 1:1 and for sample 5 a higher amount of aggregates (1:9) was determined. This higher ratio may be explained by the erosion of the binder and the higher dimension of the aggregate (8mm) (Figure 3).

Soluble salts

Samples of bedding mortars 10, 11, 12, 13 and 14 were collected from a brick masonry wall located in the Residential area in the zone farthest away of the harbour.
The samples that presented poor cohesion were prepared and extracted with distilled water and the ions chloride, sulphate, nitrate, calcium, magnesium, sodium and potassium were quantified by ion chromatography [(6)]. The results are presented in Table 4. In Figure 9 the concentration, profiles of chlorides, sulphates, nitrates, calcium, sodium, and potassium, along the wall are presented.

Table 4. Results, in miliequivalent of ions per liter in water solution

Sample	Sodium Na^+	Potassium K^+	Magnesium Mg^{2+}	Calcium Ca^{2+}	Chloride Cl^-	Nitrate NO_3^-	Sulphate SO_4^{2-}
10	0.12	0.07	0.01	0.55	0.15	0.01	0.32
11	0.17	0.04	0.01	0.36	0.15	0.05	0.07
12	0.14	0.05	0.01	0.39	0.16	0.04	0.04
13	0.12	0.09	0.01	0.28	0.10	0.01	0.01
14	0.04	0.03	0.02	0.27	0.10	0.01	0.02

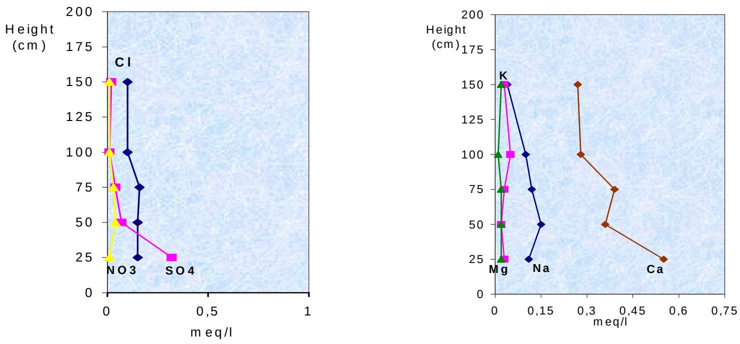


Figure 9. Concentration, profiles (in meq/l), of chlorides, sulphates, nitrates, calcium sodium, and potassium, along the wall on the residential area.

According to the shape of the profiles, the salts are clearly calcium sulphate and sodium chloride. The excess of calcium was certainly solubilised from the lime present in the mortar. Nitrates are probably coming from the chemical products that were previously used in the area to get rid of the colonising vegetation (7). The salt content is not very intense and decreases steadily from the bottom to the top of the wall. This type of salt distribution pattern is compatible with an upward migration of saline solutions through a mechanism of capillary rise.

CONCLUSIONS

Based on the characterization of the mortars of Tróia masonry, it was found that different types of aggregates are present, namely quartz, limestone and brick. The type of binder utilised was essentially lime and lime with brick powder and mortars presented a binder to aggregate ratio of 1:1 and 1:9. It is evident that the results in terms of binder to aggregate ratio reflect the actual composition, not the original one, because of curing process and the decay phenomena, which may explain the higher binder aggregate ratio of sample 5.

The ion concentrations decrease with height, suggesting that an incipient capillary rise mechanism is pumping up the saline solutions existing in the ground.

A sample representative of the type of Roman construction technology showed to be constituted of a bottom layer of clay followed by upper layers with different sizes of aggregate from coarser to finer ones, which suggests that this clay layer might have been used to give waterproof conditions to the *cetariae*.

ACKNOWLEDGEMENTS

This paper presents results obtained under the European project *PRODOMEA* (PROject on high compatibility technologies and systems for conservation and DOcumentation of masonry works in archaeological sites in the Mediterranean Area) – where a study of Roman masonry mortars to support future interventions was included.

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