An Innovative Methodological Approach for the Study of Ancient Cistern Waterproofing Mortar of Sagunto Castle

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Abstract

In this work, we present the results of the chemical, mineralogical and colorimetric characterization of the waterproofing mortars from the ancient cisterns of the Sagunto Castle (Valencia, Spain). The fortress presents 2500 years of human occupation and, given the lack of natural water sources, collecting and storing rain water was mandatory ever since. Nowadays, several cisterns are found in the hill, and thus the application of analytical approaches can help in characterizing each layer within the cultural phases of the Castle's history (Iberian, Punic, Roman, Islamic, Medieval, Modern or Contemporary). Mineralogical analyses were carried out employing X-ray diffractometry and mid-infrared attenuated total reflection spectroscopy, and, on the other hand, the portable energy dispersive X-ray fluorescence spectroscopy was employed to obtain the concentrations of major and minor chemical elements. Colour features of the samples were identified by smartphone photo processing to observe possible relation between colour and waterproofing mortar compounds. Last, Raman spectroscopy was employed to analyze the different phases present in the samples. Multivariate statistics were employed to identify different waterproofing mortar layers and develop hypotheses concerning different construction phases and compare their manufacturing processes. Analytical results allowed to find common patterns among different cisterns and mortar layers, and colorimetric analyses showed good potential as an additional fast, cheap and non-destructive source of information for studying these types of samples.

Keywords: ancient mortar, waterproofing plaster, cisterns, Sagunto castle, x-ray diffractometry

Introduction

Nowadays, Sagunto (Valencia, Spain) is a coastal city found a few kilometers North from the city of Valencia, in the Mediterranean shore of Spain. This region has been inhabited ever since the 5th century Before Common Era (BCE), and has undergone different occupations by the cultures that have passed through this area. Sagunto gained special interest during the Second Punic War (219-202 BC), when the Carthaginian army of Hannibal sieged and conquered the city (then named *Arse* by the ancient, local Iberian population), provoking a war declaration by the Romans and the starting point of the Roman conquest of the Iberian Peninsula. During the Roman Imperial period, the city, known as Sagvntvm, was rebuilt and new constructions were added like the amphitheater and the theatre. After the fall of the Roman Empire, the city was taken over by the Visigoths, who ruled the city until the Cordoba Caliphate gained control. Muslims inhabited the city for 5 consecutive centuries, until the Christian king James I of Aragon retook the city in the 13th century of the Common Era (CE). Contemporary conflicts have been also witnessed by the Castle, like the Napoleonic wars in 1811 which confronted the Spanish people versus the invasion of French troops, or the Spanish Civil Wars (1936-1939). As a consequence of these conflicts, the Castle received heavy damage (*1*). More recently, restoration efforts have been implemented in the Castle in order to consolidate, preserve and reconstruct parts of the structure (*2*).

As a consequence of the diversity of cultures and extensive occupation of the castle, their structures were built in different times, and, subsequently, reused and amended when necessary. This all results in a complex mixture of layers and construction materials overlayed on the different surfaces of the walls.

In this work, special focus is made on the waterproofing surfaces of the cisterns present in the castle. Given the orography and the climate of the region, water can be a scarce resource in some periods of the year. Thus, its collection and storage was imperative for the civilizations that lived in the castle. To it, different cisterns were built in the complex in different periods, consisting of big cavities in the rock, which were covered by waterproof layers of materials intended to isolate the cistern and avoid water leakages.

These covers were usually made out of a mixture of sand (aggregate) and lime (binder) in different proportions, and have been subjected to chemical analysis in different case studies (*3*–*5*).

Common analytical approach

Given the cultural interest and value of the analyzed archaeological samples, their study is often performed by non-destructive or slightly destructive techniques. In this context, portable spectroscopic and spectrometric techniques are usually employed. Fourier Transform Infrared Spectroscopy (FTIR) is implemented in order to study the phases present in the samples (*4*, *6*, *7*), as well as some organic components that might be present as a consequence of deposition or biological processes. Elemental composition of major and minor elements is often assessed through energy dispersive X-ray fluorescence spectrometry (XRF), a technique that has allowed for the identification of different material sources (*3*, *8*) in historical contexts like the one under investigation. Raman spectroscopy is also commonly applied to the investigation of the analyzed archaeological samples, since it provides complementary information to the one acquired by FTIR. Examples of the application of this technique are widely found in the literature, like the case study of mortars in rupestrian complexes (*5*). It is also interesting due to the possibility of identifying decay compounds in rocks and mortars (*9*), like complex organic molecules (*10*), oxalates (*9*) and amorphous carbon structures (*11*). Crystalline phases that might be present are often assessed by X-ray diffractometry (XRD) (*4*, *12*).

Techniques like Raman, FTIR and XRF have been adapted to portable devices. Portability, despite necessary for the *in situ* assessment of samples, often comes along some drawbacks, like lower sensibility and more constrained working ranges. In this sense, when employing these techniques, analysts must be aware of the limitations of the results, and a compromise between the necessity of information and the degree to which samples can be destroyed must be reached.

On the other hand, colorimetry is often overlooked when assessing the conservation state and composition of the samples. Some previous works that apply colorimetry to assess the conservation state buildings have been published (*13*), but the implementation of smartphones to this end is still to be investigated. Research on smartphone applications to the study of ancient mortars and plasters has been carried out in our lab (*14*) using a destructive approach (grinding the material), but no investigations on the direct implementation of this technique has been carried out yet.

Materials and methods

Sampling process and description

Samples were collected from the different cisterns with the pertinent allowance by authorities. Six different cisterns have been included in the study. In table 1, a summary of the sampled cisterns is provided. Each one of the six cisterns are coded with a number that indicates their position in the castle. Within each one of them, different layers have been sampled and analysed, and coded with a pattern X.Y, where X stands for the cistern and Y stands for the layer.

Prior to the analytical measurements, samples were clean by physical brushing in order to eliminate depositional contamination, and measurements were carried out on the clean surfaces.

Spectroscopic Infrared measurements were made with a portable handheld device from Agilent (4300 Handheld FTIR Spectrometer) using the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) module. Elemental composition was assessed by the means of a handheld X-ray spectrometer from Bruker (S1 Titan) using the internal calibration "GeoChem Trace". Raman spectroscopic measurements were acquired with a i-Raman Plus spectrometer (model: BWS465–785S) by B&W Tek. Laser wavelength is 785 nm, with a total power of 340 mW. Measurement parameters were as follows: acquisition time 1000 ms, 30 measurements, 5 % total power. A microscopic probe was used. Measurements were made at least twice per sample, depending on the size, in order to have representative information.

Tab. 1. Samples' description.

Cistern	Original construction	Layers' codes
3	Roman Imperial	3.1, 3.3
5	Undefined	5.1, 5.2
9	Undefined[a]	9.2, 9.3
10	Roman Imperial	10.1, 10.2, 10.3, 10.5
13	Undefined[a]	13.1
27	Pre-Roman	27.2, 27.3, 27.4, 27.5, 27.6, 27.7

[a] Cisterns 9 and 13 origins are unclear, although they are ascribed to Iberian or Roman Republican periods.

Instruments

Smartphone colorimetry was carried out using a Samsung Galaxy Edge S7 model SM-G93F, with a 12.2 MP camera sensor. Samples were introduced inside a white foam box, which was closed by a top lid. A set of LED strips was placed on the bottom part of the lid, pointing down, in order to supply homogenic illumination to the samples. A white Teflon material was used in all the images in order to control the lighting conditions fluctuations, and used as a reference white. Images were taken with the *pro* mode of the built-in camera app, with the following parameters: ISO 50, aperture 1/90, white balance 3100 K. Images, stored in *.jpg* were transferred to Matlab to carry out the image treatment steps using ColorLab toolbox (*15*). Different Regions Of Interest (ROI) were selected in the samples, focusing only on those pixels which corresponded to the agglutinant material.

Data analysis

Data analysis was carried out using R (*16*), and data visualization was done using the package *ggplot2* (*17*).

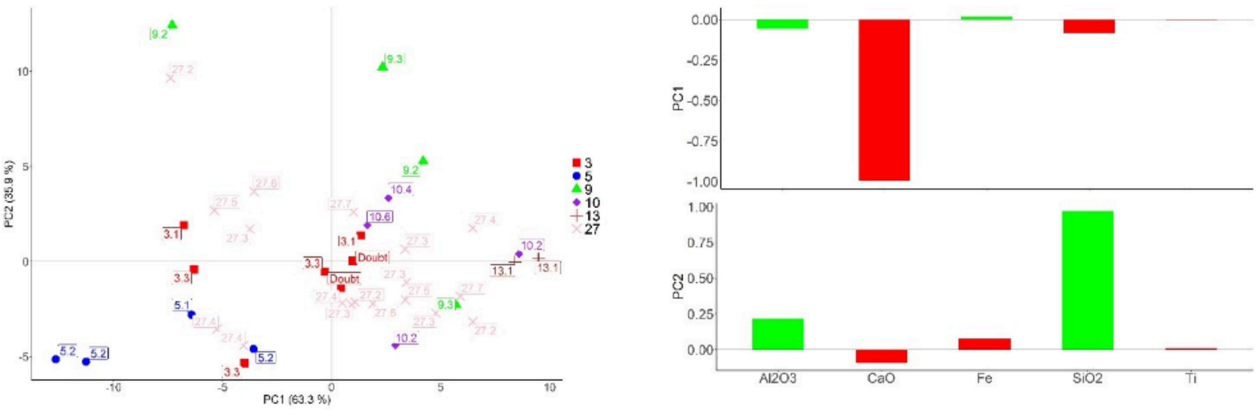
FTIR spectra were studied in the ranges from 1700 – 1900 and 2400 – 3000 cm^{-1} through a Principal Component Analysis (PCA), and two treatments were applied: Standard Normal Variate (SNV) to compensate for the scattering effects, and Savitzky-Golay filter and derivative (order 3, window length 13, 2nd derivative) to smooth the spectra. To this end, the packages *prospectr* (*18*) and *signal* (*19*) were used. XRF data was considered for Al, Ca, Fe, Ti, Si, Sr, Pb, Cu, Zn, Ni and Mn. The samples containing levels below the limit of detection were inputted as half the minimum value found for each element in the dataset. Values for the PCA were centred and scaled.

Results and discussion

Spectroscopic characterisation of the samples using FTIR indicated that the common pattern of the samples was the presence of CO_3^{2-}, shown by the presence of weak bands at 1795 and 2500 cm^{-1} (*20*), as well as a *reststrahlen* band at 1400 cm^{-1}. The application of PCA further corroborated that no separation was possible on the basis of this information, given the fact that only carbonate was observed by this technique.

When it comes to the elemental composition analysis, a first PCA was done with only major elements (Al, Ca, Fe, Si and Ti) for every cistern. As can be seen in Figure 1, the two first Principal Components (PC) are constructed on the basis of the two main components of the mortars. First, PC1 keeps 63.3 % of the total variance of the dataset, and negatively correlates to the concentration of Ca, which is mainly attributed to the lime (binder) fraction; second, PC2 keeps 35.9 % of the variance, and reflects the presence of the aggregate, mainly based on alumina-silicates.

Analysing the scores plot, some interesting considerations can be drawn. Samples from Cistern 3 are plotted around the centre of PC1, despite some samples from layer 3.3 are displayed on the positive side, indicating higher amounts of Ca. Cistern 5 is clearly plotted on the negative side of PC1, regardless of the layer, and thus high amounts of Ca-based compounds are observed. Samples from Cistern 9 are scattered around the plot, indicating a high degree of heterogeneity in the samples. Samples from Cisterns 10 and 13 are plotted on the positive side of PC1, with lower concentrations of Ca. Finally, assessing the results of Cistern 27, a high degree of heterogeneity is found.



(a) (b)

Fig. 1. (a) Scores plot for the PCA obtained by the elemental analysis of cisterns (excluding cistern 27) (b) correlation between elements and PC.

In order to assess more in depth the dataset, the relationship between Al and Si was studied in Figure 2. Once again, Cistern 27 proved to be very disperse over the scatterplot. However, the rest of the cisterns were separated based on different proportions between both elements, and more interestingly, some strata were also separated based on this relationship.

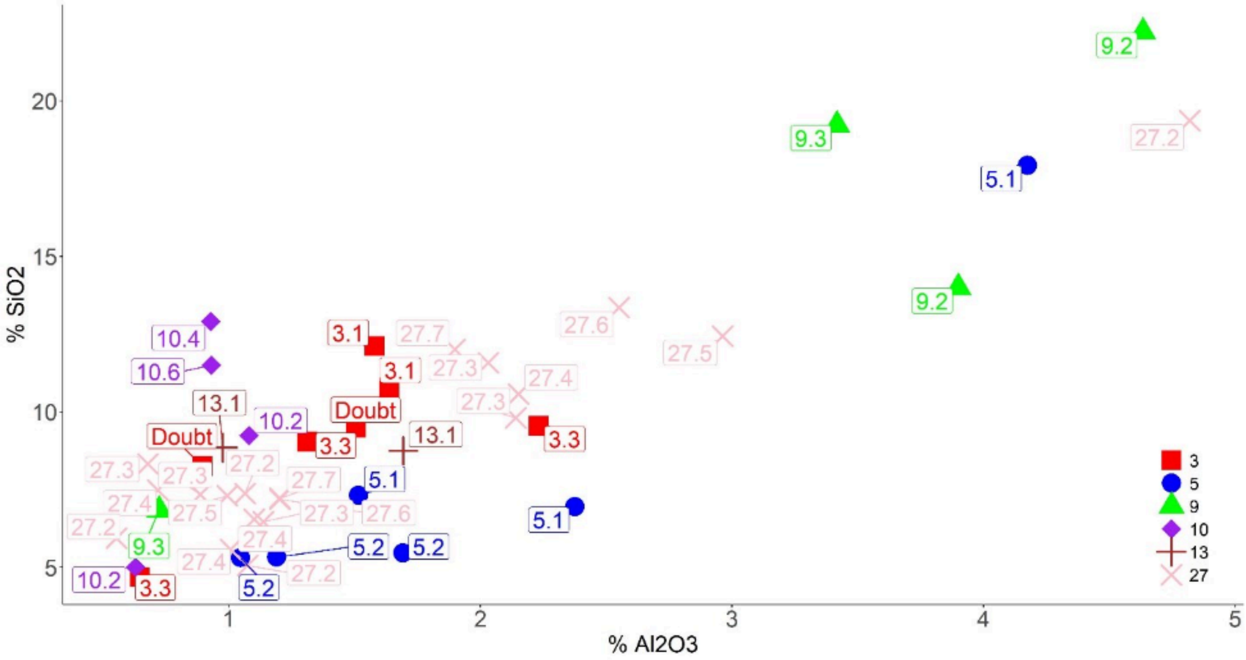
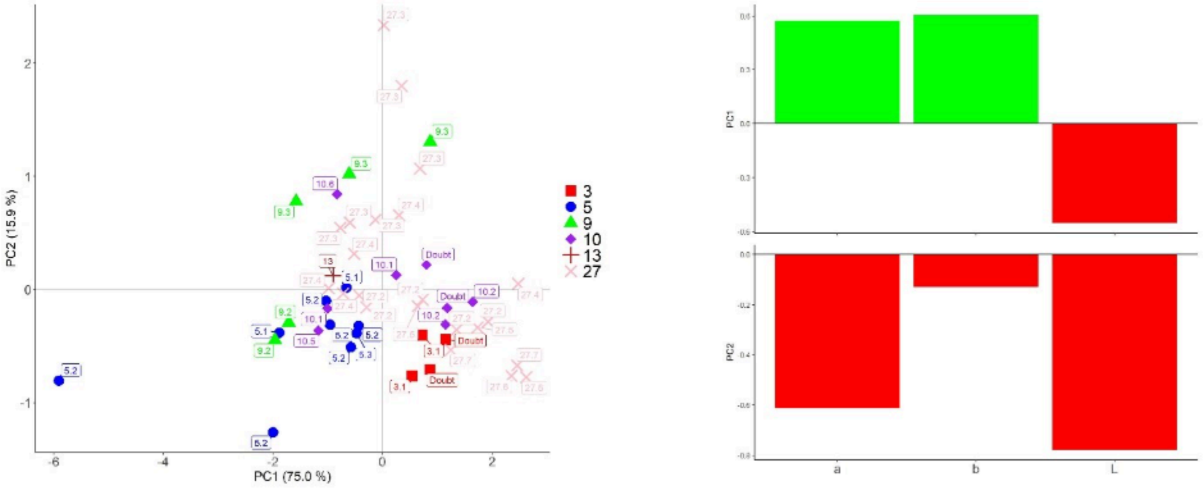


Fig. 2. Relationship between Al and Si found in the samples.

Assessing Cistern 3, samples are plotted on the intermediate part of the plot, being 3.1 higher than 3.3 in the vertical (Si) axis, and thus pointing towards a differential raw material used as aggregate. Similarly, Cistern 5 shows two differentiated strata, being 5.1 richer in Si than 5.2, while both of them are different from Cistern 3 in terms of their lower Si content. Cistern 9 shows very disperse and heterogenic composition, which could also be observed by the naked eye, and hence the scattered elemental composition. When it comes to Cistern 10, samples are found at similar levels of Si than Cistern 3, but found at lower concentrations of Al. It is interesting to mark here, as was seen in Figure 1, that Cistern 10 presented lower Ca than Cistern 3, despite both being assigned to the same historical period. This means that, probably, elements used for the mortar were obtained from different positions. Cistern 13 is found very close to Cisterns 3 and 10, and clearly differentiated from Cistern 9. This is interesting because Cisterns 9 and 13, despite being of unknown origin, were suspected to belong either to Iberian or Roman Republic periods. After this chemical analysis, it can be concluded that these two cisterns present differences in terms of their chemical composition.

The colorimetric characteristics of the samples was captured by selecting those pixels that belonged to the agglutinant, and avoiding any ceramics or inclusions. CIELAB parameters were imputed to carry out a PCA study. As observed in Figure 3,



(a)

(b)

Fig. 3. (a) Scores plot for the CIELAB PCA investigation (b) correlation between PC and CIELAB parameters.

Colour results allowed to significantly discriminate among the different cisterns. Cisterns 3 and 10 proved to be on the positive side of PC1, thus meaning that higher a* and b* components are characteristics of these samples. On the negative side of PC1, Cisterns 5 and 13 are found, characterized by lower L* (darker aspect). This time, assessing Cistern 27 finds colorimetric differences on both axis: strata 27.3 and 27.4 are found upper on PC2, while 27.6 and 27.7 are lower on PC2 and on positive values of PC1. Lastly, 27.2 finds in a middle point between the two groups mentioned.

Raman investigations on the samples revealed the ubiquitous presence of calcite, by the peaks at 153, 283, 713 and 1086 cm-1 (9, 21). Rare forms of carbonates like trona, Na3(HCO3)(CO3)·2H2O, were found in samples from Cisterns 9 and 27, given a signal at 1060 cm-1 (22).

Silicon was mostly found in the shape of quartz (205, 462 cm-1) (23), although less frequent silicates, like moganite (509 cm-1) was potentially found in one sample of Cistern 5 (24).

The presence of Ti in the samples was attributed to its structure anatase (142, 511, 635 cm-1) (25), although some samples showed two peaks (445 and 610 cm-1), which were attributed to rutile (26, 27). Anatase was found in samples from Cisterns 9, 10 and 13, while rutile was found in one sample from Cistern 27.

Iron, when found, was in the form of haematite (Fe2O3), since peaks at 226, 292, 411 and 610 cm-1 (23) were found in Cistern 13.

Gypsum (1008 cm-1) (28) was only found in a couple samples from Cistern 27.

Conclusion

In this work, a multianalytical approach to characterize ancient mortars used as waterproofing plasters in cisterns has been proposed. With the employment of FTIR, the presence of $CaCO_3$ was demonstrated, while portable XRF fluorescence allowed the identification of the two main components of mortars: Ca and Si/Al-based compounds. Based on this information, a distinction between layers with different proportions between both elements has been observed, consequence of the diverse historical periods that the castle has passed by.

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