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CHARACTERIZATION OF LIME MORTAR AND PLASTERS OF FORTRESS CONCEPCION DE LA VEGA

KARAKTERIZACIJA APNENE MALTE IN OMETOV TRDNJAVE CONCEPCION DE LA VEGA

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The arrival of Christopher Columbus in America stimulated the creation of new settlements in which the materials and construction methods coming from Spain and those existing in the area were used. The first village built was La Isabela (1494) where the Spaniards found good limestone for ashlars and were able to make lime as well as good clay for earth walls, masonry walls, etc. After La Isabela, the cities of La Vega (1495) and Santo Domingo (1498) were established. These villas still include vestiges of these building materials that are a source of information about their composition. The study is focused on the ruins of the fortress of Concepcion de La Vega that survived the earthquake in 1562 that destroyed the city. The aim of this research was to characterize the mortar and plasters of the fortress of Concepcion de La Vega on the Hispaniola Island. To determine their chemical and mineralogical composition optical microscopy (OM), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy and a thermogravimetric differential thermal analysis (TG-DTA) were used. The results showed that the major component of the mortars was $CaCO_3$ (95 %), indicating that there is lime mortar. The plaster is lime based with iron oxide.

Keywords: lime mortar, plasters, FTIR, Raman spectroscopy, TG-DTA

Prihod Krištofa Kolumba v Ameriko je spodbudil nastanek novih naselij, pri gradnji katerih so se uporabljali materiali in tehnologije iz Španije ter tisti iz lokalnega okolja. Prva s tem pristopom zgrajena vas je bila La Isabela (1494), kjer so Španci odkrili kakovosten apnenec za vogalne kamne ter za proizvodnjo apna, kot tudi glino ustrezne kakovosti za butane stene in izdelavo opečnih zidakov, itd. Po La Isabeli sta nastali mesti La Vega (1495) in Santo Domingo (1498). Tamkajšnje vile še vedno vsebujejo sledove omenjenih historičnih gradbenih materialov, ki so vir infromacij za preučevanje njihove sestave. Predstavljena študija je osredotočena na preučevanje ruševin utrdb iz Concepcion de La Vega, ki so leta 1562 prestale potres, ki je uničil mesto. Namen raziskave je bilo okarakterizirati malte in omete utrdb iz Concepcion de La Vega na otoku Hispaniola. Kemijska in mineraloška sestava je bila določena s Fourier transformacijsko infrardečo spektroskopijo (FTIR), Ramansko spektroskopijo in termogravimetrijo sklopljeno s termično analizo (TG-DTA). Rezultati analiz so pokazali, da je bila glavna komponenta malt kalcit ($CaCO_3$), katerega delež je znašal 95 %, kar nakazuje na apneno malto. Omet je apnenega izvora z vsebnostjo železovega oksida.

Ključne besede: apnena malta, omet, FTIR, Ramanska spektroskopija, TG-DTA

1 INTRODUCTION

1.1 General

It is well documented that one of the most popular materials that make up the architectural heritage of humanity is lime mortar, in a structural way joining stone or brick, used for rammed earth walls as a covering or decorative element.[1,2] Over the centuries, historic mortars have proven to be durable and well compatible with historic structural units; however, different factors (pollution, presence of water, temperature differences, presence of soluble salts, etc.) can accelerate their deterioration.[3]

The masonry walls of historic buildings degrade, depending on the traditional building materials (stone, brick, aerial or hydraulic mortars, etc.), due to the passage of time and site-specific environmental loads. However, the selection of repairs can be significantly influenced by different professionals' philosophical perspectives that can be broadly categorized as purist, pragmatist or cynic. The difference in their reporting will clearly determine alterative starting positions for repair works, with divergence in a project potentially occurring when philosophical tenets are applied.[4]

In this way, worldwide research on lime mortar and plaster of historic buildings has been carried out. One of the most interesting aspects is the possibility of determining what types of binder, aggregate or even admixture were used and what their characteristics are.[5–8] RILEM TC 167-COM has made crucial headway in characterizing historic masonry in chemical, mineralogical, physical and mechanical ways.[9]

Durability is one of the most important properties that a builder looks for in lime mortar. The durability re-

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fers to the ability of a structure to maintain substantially its original appearance, strength and soundness for many years. In masonry the two prime requisites for durability are a dimensionally stable unit and mortar that forms a permanent and complete bond, thereby making the structure watertight.[10]

Lime mortar and plaster have been investigated to improve the knowledge of how to make them as durable as before the cement technology was developed.[11] The durability of lime mortars is directly related to their physical properties and porosity, and there are numerous studies about the physical properties of lime mortars. Thirumalini et al. studied the influence of an addition of an organic admixture on different properties of mortars.[12] Cultrone et al. and Ponce-Antón et al. studied the manufacturing technology and durability of lime mortars.[13,14]

In America there have been few studies on lime mortars and plasters, and most of them have been carried out in Mexico. Carran et al. analyzed the first use of lime by the Mayan civilization[2]; Rodríguez Pérez et al. studied the physical/mechanical properties of the limestones from the Yucatan churches[15] and Miriello et al. assessed the hydraulicity of the lime plasters from Teotihuacan.[16] In Brazil, Gleize et al. characterized historical mortars[17]; Loureiro et al. studied the historic mortars[18] and Gomes de Oliveira et al. investigated the mortars and clay bricks in historic structure from the 18th century.[19] In Peru, Morillas et al. carried out the characterization of restoration lime mortars and decay by-products in the Meditation area of the Machu Picchu archaeological site.[20]

In the Caribbean, there are no known studies on historical mortars from the 16th century, although the first mortars were made in the West Indies with the European technology because the indigenous people of these islands did not know about it and it was the European conquerors and colonizers who introduced it. The first constructions with mortar were made during Columbus' Second Voyage in 1493, in the city of Isabela, on the island of Hispaniola. Then, between 1494 and 1495 a series of fortifications were founded in the interior of the island, among them La Concepción de la Vega. Around it, the first mining town in America was established, which was later destroyed by an earthquake and abandoned. In this village a fortification of bricks and lime mortar was built that still includes the original materials to be studied. For these reasons the aim of this research is to characterize the mortar and plasters of the fortress of Concepcion de La Vega, built at the beginning of the 16th century on the Hispaniola Island. The analysis is based on optical microscopy (OM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and thermogravimetric differential thermal analysis (TG-DTA).

1.2 Fortress of Concepción de La Vega

In 1502 Nicolás de Ovando arrived to the island as the governor of the territories discovered up to that moment. He had orders to occupy all the island's territory and established several cities. He brought many masons with him for building works, as well as some construction materials such as nails, wooden beams and bricks. The town of Concepcion de la Vega was established in 1494 but was relocated in 1504 about 2 leagues away from the original site by Governor Ovando, to the current location of the ruins. The city had a fortress whose construction began around 1511 and was completed a few years later, a gold foundry, a church that later became the cathedral, several houses and a monastery. In 1562 an

Figure 1: Current state of the tower

Figure 2: Current state of the fortress

earthquake destroyed the city and it was moved again, to the current location. When the city and the fort were abandoned, the site currently known as "Vega Vieja" was used as a "brick quarry" to construct new buildings in the new settlement of the city. The Church of Santo Cerro, built at the end of the 19th century, on the outskirts of the old city, was constructed using the bricks extracted from the ruins of the fortress of La Concepción de La Vega.

The fortress of the Conception was a rectangular enclosure of approximately 44 m × 21 m, with brick walls of approximately 1.67 m in width (2 varas castellanas) and two cylindrical towers with walls of 1.75 m in width placed diagonally opposite each other (**Figure 1**).

The existing tower has an outer diameter of 8.95 m, an inner diameter of 5.35 m and more than 4-m high, built-in brick masonry with 6 flared loopholes. The fortress had in its interior a tower of two levels that served as the residence of the warden and other dependencies. Today only one of the towers, parts of the outer wall and parts of the walls of Torre del Homenaje remain (**Figure 2**).

2 EXPERIMENTAL PART

The analysis was performed on two samples that were taken from the ruins of the fortress tower of Concepción de La Vega: F1 is a mortar sample and F2 is a plaster sample (**Figure 3**). The techniques used were:

- Optical microscopy (OM)

A general view of the samples was provided by analyses with a Nikon (SMZ800N) stereomicroscope.

- Fourier transform infrared spectroscopy (FTIR)

FTIR measurements were performed by means of a Bruker Vertex 70V spectrophotometer, in a range of 400–4000 cm^{-1}. The samples were prepared with the KBr pellet method (100 g sample/400 g KBr) in vacuum desiccators under a pressure of 1.33 Pa (0.01 torr).

Figure 3: Location of the samples

- Raman spectroscopy

In this study, Raman spectra were obtained using a RM 2000 Renishaw equipped with a Leica microscope. The excitation source was a laser emitting at 633 nm. The laser output power was 25 mW. The spectra were obtained in the 400–4000 cm^{-1} range, with a resolution of 4 cm^{-1}. The acquisition time was 10 s, and 5 acquisitions were performed to improve the signal/noise ratio. The equipment was calibrated with the ± 520.6 nm band of Si. The utilization of Raman provided valuable understanding of the chemical and physical properties of the mortars and plaster.

- Thermogravimetric differential thermal analysis (TG-DTA)

Thermal gravimetric analyses (TG-DTA) were carried out with Q600 TA instruments that measure the heat flow and weight changes in a sample as a function of temperature (or time) under a controlled atmosphere. The samples were heated from ambient temperature over a range of 25–1000 °C at a heating rate of 10 °C/min and nitrogen was used as the purging gas at a flow rate of 0.833 mL/s (50 mL/min).

All these analyses are compatible and complementary.

3 RESULTS AND DISCUSSION

3.1 Optical microscopy

Figure 4 shows a general view of the samples. In the case of mortar F1 (**Figure 4a**) small black points indicate the presence of the aggregate with a very low size.

Plaster F2 (**Figure 4b**) shows red particles that can indicate the presence of iron oxide.

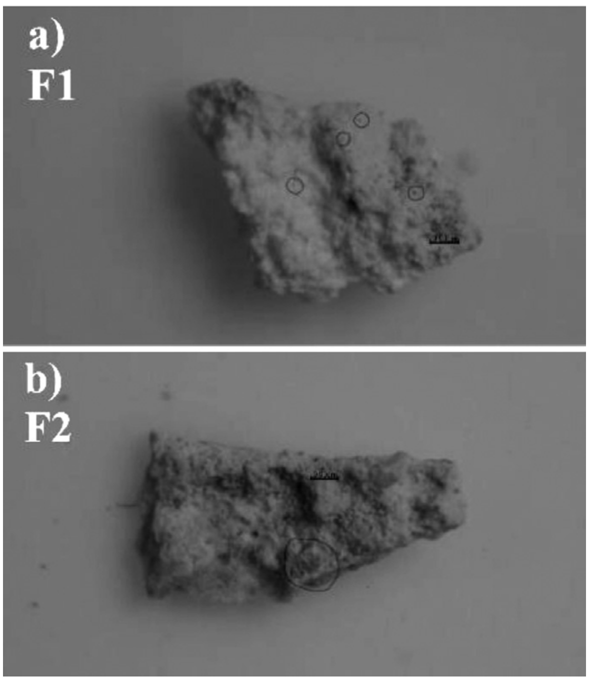

Figure 4: General view of the samples: a) mortar (F1), b) plaster (F2)

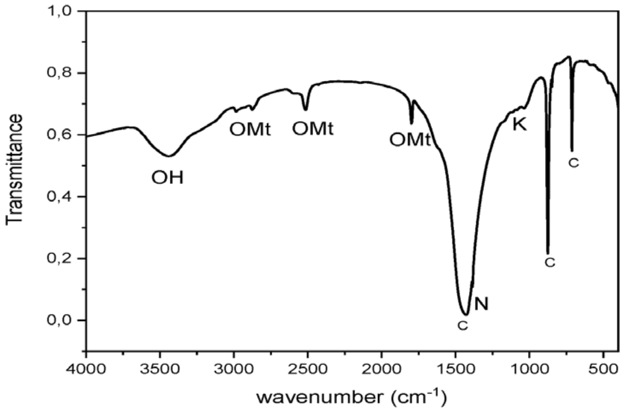

Figure 5: FTIR of the mortar (F1): C – calcite, K – kaolinite, OH – OH from water molecules, N – nitrates, OMt – organic matter

3.2 Fourier transform infrared spectroscopy

Figures 5 and **6** show the FTIR of mortar F1 and plaster F2, respectively. The mortar sample shows the following main characteristics: vibration bands of the CO_3^{2-} group present in calcite, a strong band at 1431 cm^{-1} from stretching vibrations, as well as two narrow bands from bending vibrations[21] at 870 cm^{-1} and 712 cm^{-1}. Additionally, small bands from kaolinite at (1030, 1077 and 1117) cm^{-1} were identified.[22] Signals due to the presence of organic matter probably coming from contamination were also observed, as well as a small signal at 1387 cm^{-1} due to the presence of nitrates.

The plaster sample also shows calcite and kaolinite; however, for this sample the bands from kaolinite have a higher intensity than for the mortar.

3.3 Raman spectroscopy

The Raman spectrum of the plaster (F2) is shown in **Figure 7a**, where the main bands can be attributed to iron oxide in the form of hematite (α-Fe_2O_3) and there is

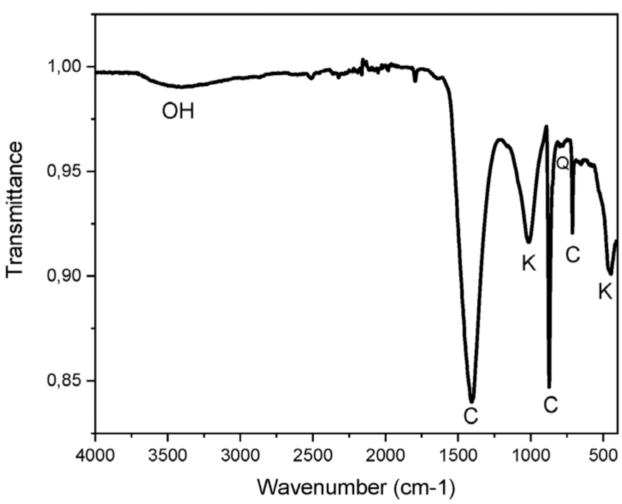

Figure 6: FTIR of the plaster (F2): C – calcite, K – kaolinite, OH – OH from water molecules, Q – quartz

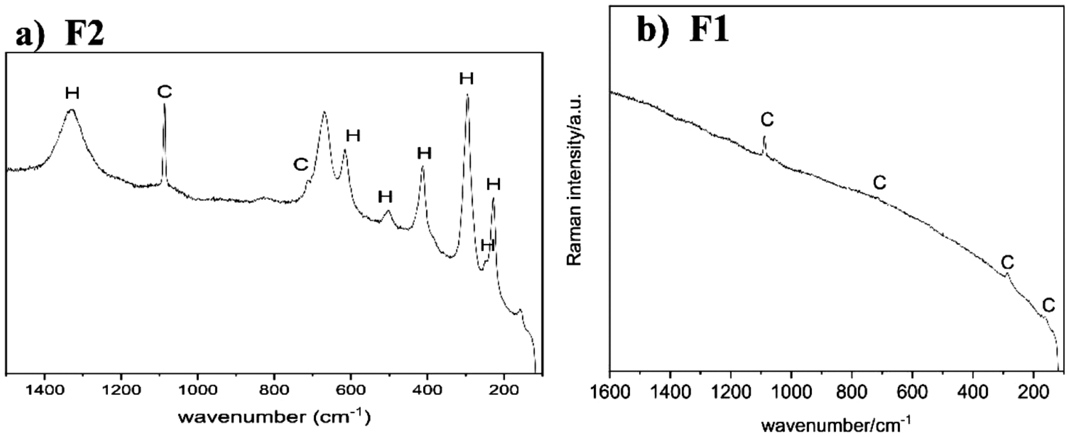

Figure 7: Micro-Raman spectra of the samples: a) plaster (F2), b) mortar (F1) (C – calcite, H – hematite)

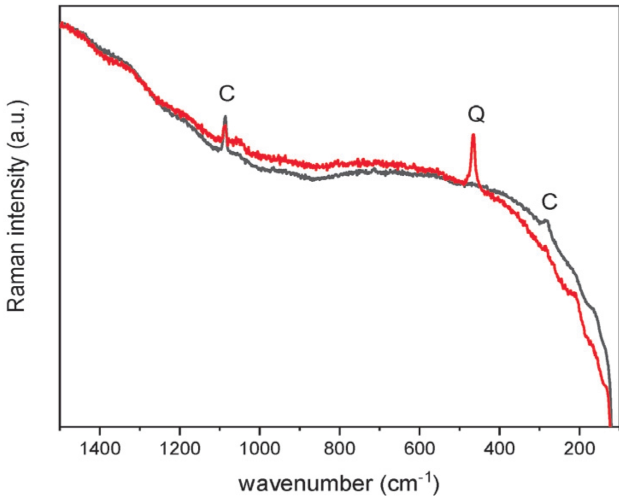

Figure 8: Micro-Raman spectra of the aggregates present in the mortar sample (F1) (C – calcite, Q – quartz)

a sharp band at 1085 cm^{-1} indicating CO_3^{2-} present in calcite ($CaCO_3$). The spectrum also shows a signal at 668 cm^{-1} whose origin is uncertain. Bikias et al. and other authors associate it with the Al-O-Si bond in kaolinite,[23] while Aguayo et al. and some other authors assign it to magnetite, an iron oxide present in igneous and metamorphic rocks.[24]

In the case of mortar (F1), only signals indicating calcite are identified (**Figure 7b**).

Figure 8 shows the Micro-Raman spectra of two different aggregates of the mortar (F1), showing that both calcite and quartz were used.

3.4 Thermogravimetric differential thermal analysis

In order to determine the amount of calcite present in the mortar (F1), a DTA-TG was performed and the results are presented in **Figure 9** and **Table 1**. The mortar

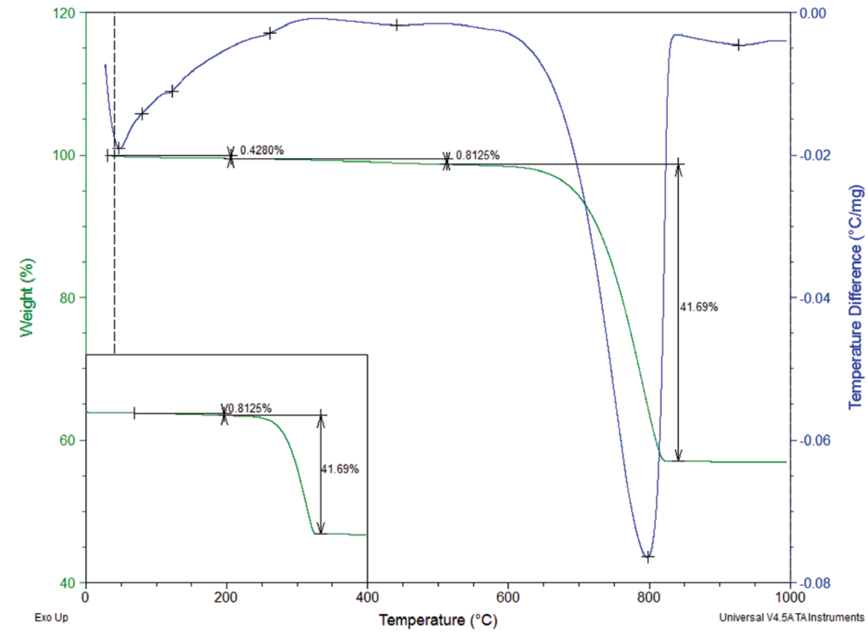

Figure 9: DTA-TG analysis of the mortar (F1)

Table 1: Weight losses of the mortar (F1) determined with TG

Temperature interval (°C)	Mortar (F1)	CO_2/H_2O ratio	Reaction
25–200	0.513	33.6	hygroscopic water and calcium sulphate dehydration
200–600	0.638	–	goethite transformation into hematite, kaolinite dehydroxylation
600–850	0.411	–	calcite decarbonation

sample (F1) shows seven endothermic peaks. In ranges of 70–130 °C and 110–180 °C, the weight loss due to water of the crystallization of calcium sulfate hemihydrate and dihydrate, respectively, takes place.[25] The peaks are very small so they are probably due to atmospheric pollution. The two peaks in the interval of 200–500 °C are attributed to the goethite transformation into hematite and dehydroxylation of kaolinite, respectively. The main endothermic peak at 797 °C with a mass loss of 41.69 % is attributed to the decarbonation of calcium carbonate. Finally, the endothermic peak at 929 °C, without any weight loss, is possibly due to the crystallization of the new high-temperature phases such as clay minerals.[26] The weight loss in the interval of 600–800 °C is 41.96 % of CO_2, which corresponds to 95.4 % of $CaCO_3$. These data indicate that the main compound in the mortar is calcium carbonate with small amounts of goethite and kaolinite, which are probably impurities from the calcite.

4 CONCLUSIONS

Through chemical and mineralogical analyses, the lime mortar and plaster of the Fortress of Conception de La Vega, the first mining town in America, was characterized. As in most constructions, the selection of the raw materials for the preparation of mortars was based on the geology of the area. The analysis indicates that the binder in the mortar is calcium carbonate, with the calcium carbonate also being the aggregate. The small amounts of gypsum and nitrates found can be from atmospheric pollution.

The plaster is also formed with calcium carbonate but with kaolinite and hematite as the additives.

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