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ANCIENT XVI CENTURY MORTAR FROM THE DOMINICAN REPUBLIC: ITS CHARACTERISTICS, MICROSTRUCTURE AND ADDITIVES

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ABSTRACT

Characterization of a mortar from the XVI century found in the colonial district of Santo Domingo (Dominican Republic) led to discovery of its composition (lime mortar), the binder/aggregate ratio (1:4), identification of the aggregates (quartz and calcite) and its additives (fats). Based on this study, and together with a microstructural SEM/EDX analysis of the mortar in which CSH type crystals were also detected, hypotheses can be established for the type of manufacture and raw materials used, and also opinions related to its durability. X-ray diffraction, infrared spectroscopy, differential thermal analysis, optical microscopy and scanning electron microscopy with EDX have been the main techniques employed.

Introduction

During rehabilitation work on the Hispanic Cultural Center building located in the colonial district of Santo Domingo (Dominican Republic), one of the walls was uncovered bordering on the Gorjón College, which dates from XVI century, and is located partly within the garden area. Over the years, various renderings had been applied to the original masonry wall.

In this study an analysis is made of the characteristics and microstructure of the mortar from the original XVI century wall. Until now, no data or references were known for this type of identification work on ancient mortars in the Dominican Republic.

Experimental

The carried out investigation was intended to identify both the chemical and mineralogical composition of the mortar. The methodology was established in a previous paper (1). The analysis was carried out on both the mortar and on the binder and aggregates once these had been separated from the mortar. Different instrumental techniques were used for the analysis: optical microscopy, scanning electron microscopy (SEM) with X-ray energy microanalysis (EDX), X-ray diffraction (XRD), thermal analysis and infrared absorption spectroscopy (IR). Both the analysis and identification of the additives were done by a treatment to extract the organic compounds and later identify them using IR spectroscopy.

Results and Discussion

Description of Mortar. Observation of the mortar, both visual and by optical microscopy, indicated that it was formed by a homogeneous mass, beige in colour, with grains of siliceous aggregate and black coloured particles of various sizes, similar to those of the aggregate, disseminated in the mass. These were carbonaceous particles that originated during the burning of the calcareous stone to obtain the lime. Clayey particles were also observed. Eventually the presence of salts (potassium sulfate) was detected. There was good adherence between the aggregate and the binder. The calculated binder/aggregate ratio is 1:4.

Chemical Analysis. The chemical analysis of the mortar, carried out in accordance with the methods described in European standard EN 196-2, are given in Table 1.

The most significant amounts found in the chemical composition of the mortar are expressed by the insoluble residue (Ins.R), the loss on ignition (LOI) and the CaO content.

The insoluble residue was obtained by acid attack using hydrochloric acid followed by ignition at 975 ± 25 °C. The result obtained for the Ins.R is very high (60.7 %) and is related to the nature of the aggregate that forms a large proportion of the mortar.

The high value (13.4 %) of the loss on ignition (LOI) (calcination residue at 950 ± 50 °C for 1 hour) can be directly related to the loss of water within the structure and the emission of CO_2. This value which together with the percentage of calcium oxide reaches 15.4 %, appears to indicate the presence of calcium carbonate in the sample and can be proved later through the application of instrumental techniques.

Aggregate Characterization. The aggregates are of a predominantly siliceous nature. The mineralogical compounds were identified, following separation from the mortar, by analysis using X-ray diffraction: quartz (Q) (main compound) and calcite (C), with dolomite traces (D) (Fig. 1).

The aggregates show good adherence to the mortar, as can be observed from the SEM micrograph in figure 2, where a grain of aggregate coated with the mortar is shown. X-ray semiquantitative microanalysis by EDX gave the following composition: SiO_2: 86.4 %; Al_2O_3: 3.5 % and CaO: 10.1 %, which corroborates its predominantly siliceous nature.

The granulometric distribution of the aggregates indicates a predominance of sizes about 1 mm, followed by 0,5 mm. The curves obtained are shown in figure 3.

Microstructural Characterization and Mineralogical Composition of Mortar. Identification of fines in the mortar revealed the mineralogical composition of the binder. First of all, through IR spectroscopy (Fig. 4) a mainly calcium carbonate ($CaCO_3$) composition, principally in the form of calcite, is observed, identified by its main absorption bands with maxima at 2520, 1420, 875, 715, 315 cm^{-1}. Absorptions due to the presence of water were also detected: region around 1640 cm^{-1} corresponding to the H-O-H bending vibrations, and in the region around 3400 cm^{-1} due to the OH stretching vibrations. The weak absorption around 1040 cm^{-1} (bending vibrations

TABLE 1
Chemical Analysis of the Mortar

Determination	LOI	Ins.R	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
wt. %	13.4	60.9	4.9	1.9	1.7	15.4	0.5	0.1

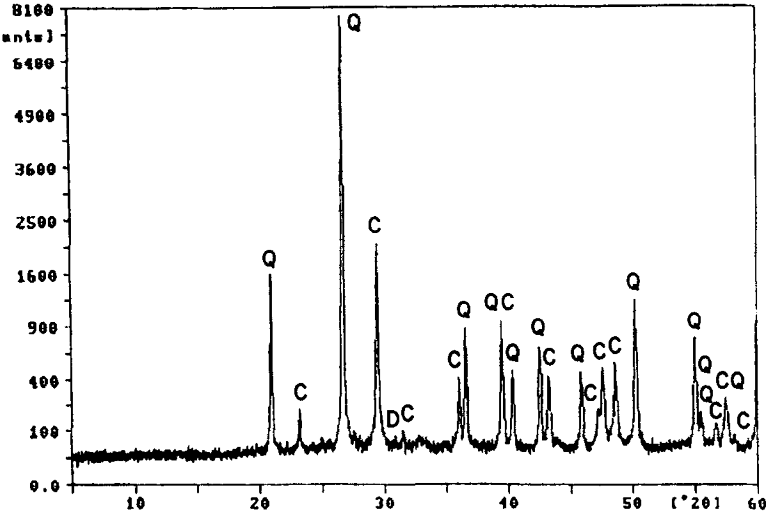

FIG. 1.
XRD of aggregate. Q: quartz; C: calcite; D: dolomite.

region due to SiO_4) reflects of the presence of silicates. Absorptions within the range between 2800 and 3000 cm^{-1} reveal the presence of organic compounds since these absorption bands are identified with aliphatic chains. Later an identification was carried out of the type of additives included in the mortar. The X-ray diffraction technique corroborates the presence of calcite (C) in the mortar (Fig. 5).

An analysis of the mortar by scanning electron microscopy revealed a mainly calcium carbonate composition, whose morphology is given in the SEM micrograph of figure 6. Its composition was determined by EDX: SiO_2: 7.1 %; Al_2O_3: 9.9 % and CaO: 83.0 %. Calcium carbonate crystals can be seen at the magnification of the SEM micrograph in figure 7. The

FIG. 2.
SEM micrograph of the mortar showing the aggregate.

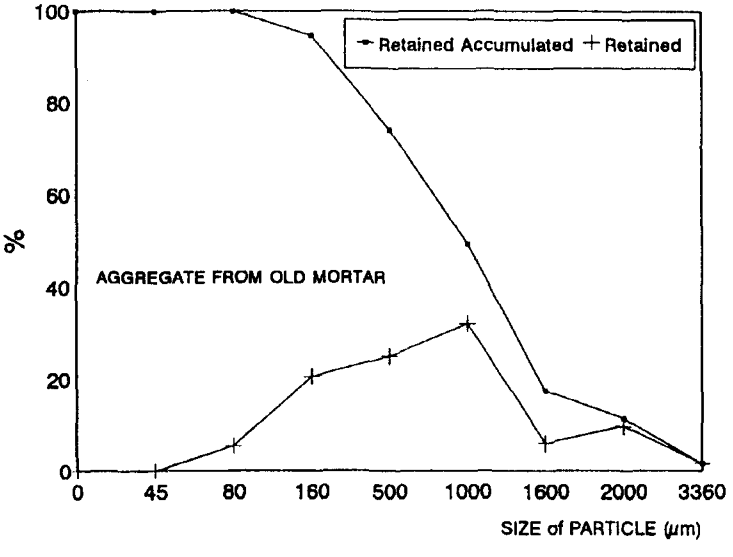

FIG. 3.
Granulometric curves of aggregate.

aggregate is identifiable within the matrix (Fig. 2). The carbonaceous particles (Fig. 8) possess high porosity and their morphology reveals that they came from the wood used for burning.

Inside the matrix of the mortar some large pores could be seen, coated by needle-shape crystals, as shown in the SEM micrographs in figures 9 and 10. The SEM/EDX microanalysis of this zone indicates that it is principally composed of Ca and Si with a Ca:Si ratio higher than 1 (about 1.3:1). This is a network fibres of the tobermoritic type.

Through an analysis using X-ray diffraction, it was possible to detect the presence of peaks assigned to hydrated calcium silicates of the C_2SH - CSH type (*) (Fig. 5), even when the peak with the greatest intensity due to the calcite overlaps with the principal peak of these silicates.

Per S.L. Sarkar (2) these formations of CSH - type crystals in the lime mortars probably result from the burning of lime and clayey material.

The inclusion of clayey materials in ancient lime mortars, and also in gypsum mortars (1), was a common practice in Spain particularly during the Middle Ages, as is revealed in many unpublished studies carried out for the restoration purposes; however up to now these crystalline formations in XVI century mortars had not been found. In this case, a hypothesis has

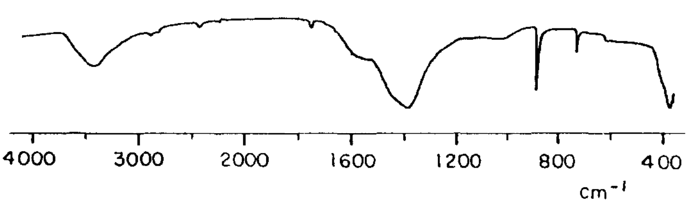

FIG. 4.
IR spectrum of the fines in the mortar.

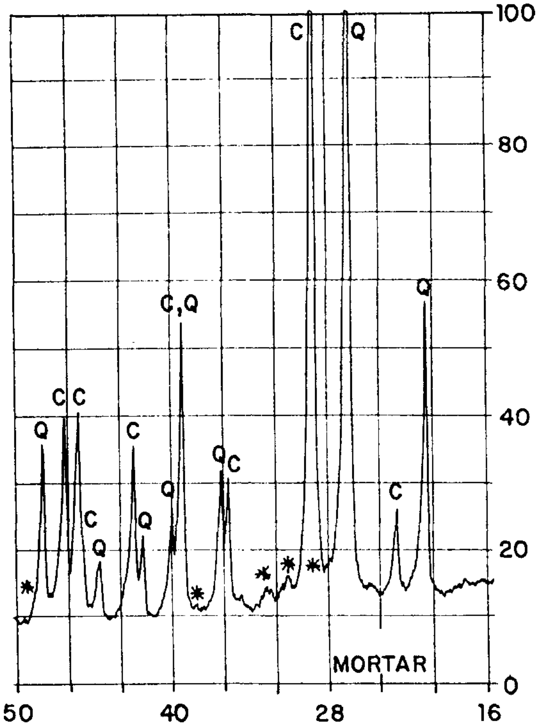

FIG. 5.
XRD of the mortar. Q: quartz; C: calcite; *: CSH type.

been established indicating that the calcareous stone used as raw material in the preparation of the mortar studied, contained clayey impurities, which is plausible in the Dominican Republic, and was subjected to thermal treatment. The proportion of silicates found in the mortar is small (Figs. 4 and 5).

FIG. 6.
SEM micrograph of the fracture surface of the mortar.

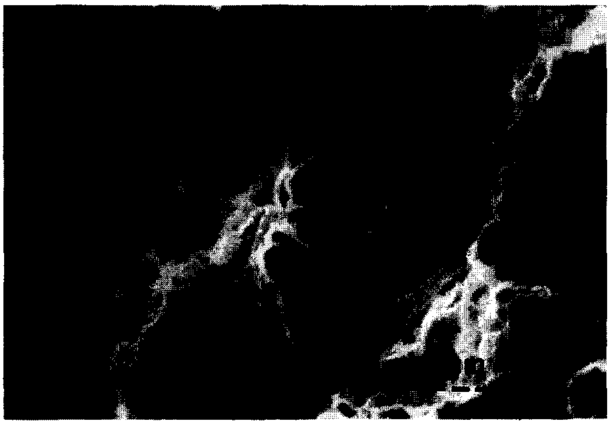

FIG. 7.
Calcium carbonate crystals formed in the lime mortar. Higher magnification micrograph from the center of area shown in FIG. 6.

The differential thermal analysis patterns of the fine material of the mortar (Fig. 11) show presence of water in the structure and two endothermic peaks at 566.8 °C, due to quartz, and at 776.5 °C due to carbonates. The exothermic peak at 894.3 °C is relationed with the calcium silicate hydrates and it is due to the conversion into wollastonite (3). The exothermic temperature increased with the rising Ca/Si ratio up to 900 °C for 1.5 ratio. T. Mitsuda and et al. (3) also observed another weak one at about 800 °C for Ca-rich C-S-H higher than 1.3 ratio (Fig. 11).

Additives. Natural products were used as mortar additives in ancient times. J. & N. Ashurst (4) exposed the traditional additives in the British Isles.

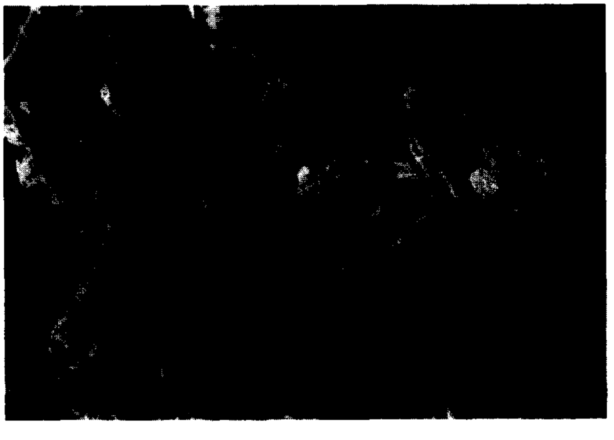

FIG. 8.
Morphology of the carbonaceous particles.

FIG. 9.
A large pore showing needle-shape crystals of CSH - type.

The organic compounds detected in the mortar (Fig. 4) were analyzed using IR spectroscopy, following extraction from the mortar by means solvents.

The existence of abundant fat was identified in the extraction residue, and also a small amount of calcium soap (5) (Fig. 12). This means that a quantity of fat or oil was added to the mortar during mixing, that caused a small reaction with the lime of the mortar. This was a common practice of the era in Spain, for both lime and gypsum mortars (1).

Conclusions

The XVI century mortar from Santo Domingo (Dominican Republic) was prepared with a 1:4 mixture of lime and sand, composed mainly of quartz and calcite grains. The remains of

FIG. 10.
Higher magnification micrograph from the center of the FIG. 9.

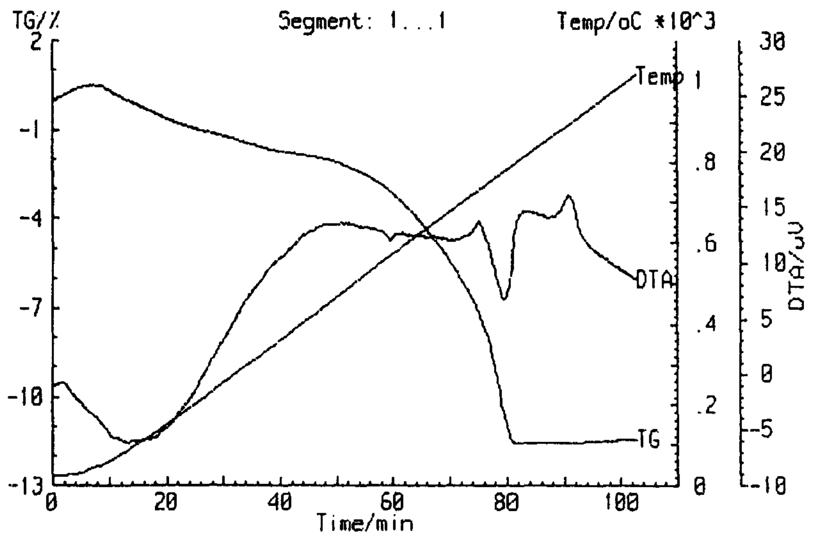

FIG. 11.
Differential thermal analysis of the ancient mortar.

carbonaceous particles disseminated throughout the mortar indicate that the lime used as raw material was first burnt in a wood-fired furnace.

As was normal practice during that age, additives that have been identified as fats were included in the mortar.

The mortar has a good performance over the years, during which it has had high levels of humidity and variable concentrations of soluble salts.

The presence of CSH type crystals may indicate that the calcareous stone used to prepare the lime for the mortar contained clayey materials.

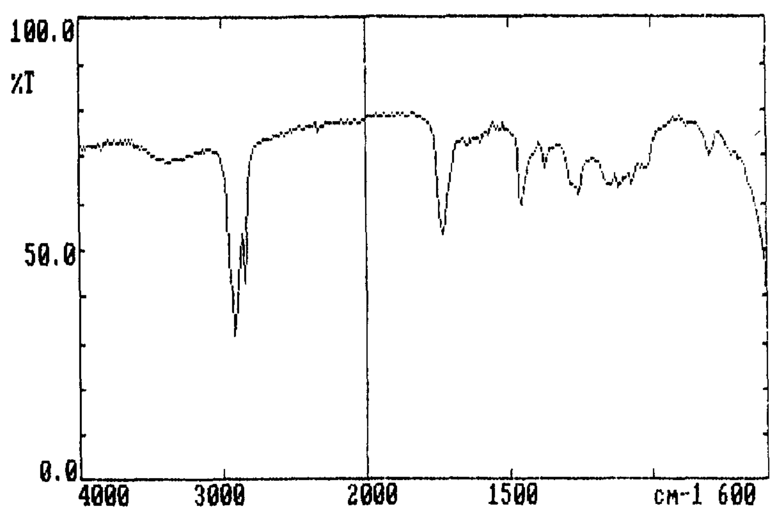

FIG. 12.
Additive of mortar IR spectrum of extracted residue.

The characteristics and technology of this Dominican mortar from the XVI century (lime mortar, binder/aggregate ratio, composition and granulometry of aggregates, raw lime preparation, use of additives,...) are similar to those of European mortars (6) that followed the Roman tradition (7) and are found in Spanish monuments of the same period, demonstrating a transfer of technology to the American shores.

Acknowledgments

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