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CHEMICAL AND PHYSICAL CHARACTERIZATION OF STUCCOS FROM A MEXICAN COLONIAL BUILDING: EL MUSEO DEL CALENDARIO OF QUERETARO*

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Restoration requires the use of appropriate characterization methods and suitable new material preparation processes permit the reproduction of the original material to be as similar as possible in order to be an appropriate application method. The combination of these factors will facilitate a good restoration process. Different stuccos were taken from El Museo del Calendario, a building located in Querétaro, Mexico which was built in the 16th century. All the stucco samples were studied using the characterization process which is proposed in this article. The characterization method consisted of the use of analytical techniques, such as X-ray diffraction, Fourier transform infrared and scanning electron microscopy. This characterization method made reproduction of the original material possible. The new material combined with new application techniques developed in situ *will result in a high-quality restoration process.*

KEYWORDS: STUCCO, CHARACTERIZATION, HERITAGE PRESERVATION, RESTORATION, LIME

INTRODUCTION

Many ancient structures around the world were made using chemical compounds of the lime-cycle, which were used until the end of the 18th century. Lime plasters and stuccos and lime mortars as binder for stones and bricks were the main cementitious materials in masonry structures. Recently, ordinary Portland cement (OPC) has become the most commonly used binding material, demonstrating certain advantages over lime composites, such as shorter setting and hardening times, with higher mechanical properties. However, using OPC on old structures has some serious undesirable effects due to the differences in its toughness, rigidity, impermeability and thermal expansion coefficient properties (Elert *et al.* 2002).

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OPC is the main component of modern plasters, sometimes with the addition of acrylics and glass fibres. Organic and inorganic additives in stuccos and mortars have been used in order to improve or add other properties to the original behaviour of these mixtures. The use of these additives varies in relation to locations and times, mainly due to their availability, quantity, cost and their desired effect. In the case of additives, some of these effects include accelerated setting and greater strength, better adhesion, frost resistance, more versatile workability, setting retarders, and water proofing. Velosa and Veiga (2002) and Moropoulou *et al.* (2004a,b) have reported that the addition of the reactive siliceous source, pozzolan, with lime and water, produces a string of hydrated calcium aluminates and calcium silicates caused by the hydraulicity of the follow-on mortar. Combined, these materials create better mechanical properties compared to air–lime compounds.

The practice of conservation of cultural heritage dates back as far as 1534. Pope Paul III established regulations regarding the work on classical monuments of Rome, as well for the control of exportation of antiquities and artistic objects (Ridley 1992). Later, similar regulations were established in several European countries. In 1803 King Charles IV of Spain approved the royal ruling that protected archaeological findings and ancient monuments, in order to preserve the antiquity and honour of the towns where they were located (Maier Allende 2003).

Appropriate restoration requires three key components: the first is related to the study of the elemental composition of plasters, stuccos and mortars. This implies a knowledge of crystalline phases, elemental composition and mechanical properties, to mention but a few (Galván-Ruiz *et al.* 2007). The second is related to the technology employed to reproduce the original material to be used in the restoration process. And the final one is the reproduction and development of techniques for applying stuccos and mortars.

With regards to application techniques, there are two key points: the expertise of the technician and the relationship between the old surface and the mortars or stuccos that will be applied in order to avoid or reduce incompatibility. The study of workability of the fresh state of the mixes is very important in order to obtain a suitable degree of mix handling. In the long run these factors will affect the behaviour of the hardened paste, its shrinkage, porosity and microstructure (Casadio *et al.* 2005). There are also other factors to take into account, such as the binder–aggregate composition ratio and the kneading water content, as well as type and amount of added mixture. The most important factors are the rheological parameters for these mixes, which tend to react according to the behaviour of a Bingham model and are the relative yield stress and the relative plastic viscosity (Seabra *et al.* 2007).

In a modern restoration process it is common to find a mixture of materials that will often eventually produce undesirable reactions. The most common case is the simultaneous application of cements and epoxy or acrylic resins. This problem may originate due to a lack of knowledge of the lime compounds and the technology thereof.

This article focuses on the study of ancient stuccos from a Colonial building located in Querétaro, Mexico. The objective is to accomplish a restoration process following the guidelines as stated by the National Institute of Anthropology and History (INAH). This is the Mexican ministry that establishes the codes and procedures for maintenance and restoration of cultural heritage in Mexico. These restoration efforts took into account the principles of restoration (Articles 9 to 11) of the International Charter for the Conservation and Restoration of Monuments and Sites (The Venice Charter 1964), presented in the Second International Congress of Architects and Technicians of Historic Monuments, Venice, 1964.

The mineralogical and chemical composition, along with the texture and microstructure, must be analysed in order to understand the procedures required to produce the final product and the nature of the adhesion bonds (Moropoulou *et al.* 1995, 2003). A complete physical and chemical characterization of stuccos was carried out. Fourier transform infrared was used to identify mineral constituents contained in the stuccos. X-ray diffraction was employed to identify crystalline phases of the mineral components. Scanning electron microscopy (SEM) images were used to study the morphology, microstructure and the interaction of the different components in the material blends that form ancient stuccos and crystal growth habits of the mineral components. By means of SEM-energy dispersive spectroscopy (EDS), it was possible to identify the constituent elements of the ancient stuccos. The aforementioned analytical techniques (listed above) are commonly used in materials science to study new materials. These techniques create an in-depth knowledge of the original composition of stuccos in the first step of a successful scientific restoration process.

MATERIALS AND METHODS

Building description

Following a battle without arms between the native Otomíes and the Spanish conquerors in 1531 which lasted only hours, the first city planning regulations were passed in 1538. In this document, guidelines for the construction of churches, streets and government buildings were laid out. Querétaro obtained the title of 'Village' in 1606, and in 1655 received the title 'Very Noble and Royal City' whose proposed layout symbolizes its multi-ethnic population. It was also endowed with a wealth of extraordinary buildings, notably during the 17th and 18th centuries. On the oldest city map available, from the year 1760, the block where El Museo del Calendario is located can be seen on the city property plans. On newer city maps, which have been available since 1778, the front part of this house is already visible; indicating that some of the stuccos and mortars studied in this project correspond to this period (see Fig. 1). According to archaeological findings during this restoration process, this building underwent at least three different modifications from the front to the back (Fig. 2). Some walls were made of adobe, part of the first period, others of stone in the second period, and the rest, called '*muros de miseria*' or misery walls, which can be found in the third and last period of construction at the end of 18th century, were made with a mixture of stone and bricks in a random order.

The front of the building prior to the intervention can be seen in Figure 3. Regardless of the preserved appearance, the main wall had several damaged areas of separated stuccos and large cracks along the top of the walls. In addition, the main door was in an advanced state of deterioration. The particular surroundings of the building can be observed at the top of the Figure 4. Some rooms, corridors and part of the patio of stage I, are included in the image.

Stucco sample collection

In order to obtain a complete identification of all mineral components incorporated in stuccos and mortars, six stucco samples were taken from three different locations of the house, corresponding to the three construction phases, and studied (see Fig. 2). Samples F1 and F2 correspond to stage I, samples C1 and C3 to stage II, and C4 and C5 to stage III. The samples collected weighed approximately 250 g and were gathered from selected sites of these walls where no prior interventions had been made. These were stored in sealed bags for later analysis. The exterior surfaces of the locations where each of the stucco samples was taken were removed because they contained a coloured layer.

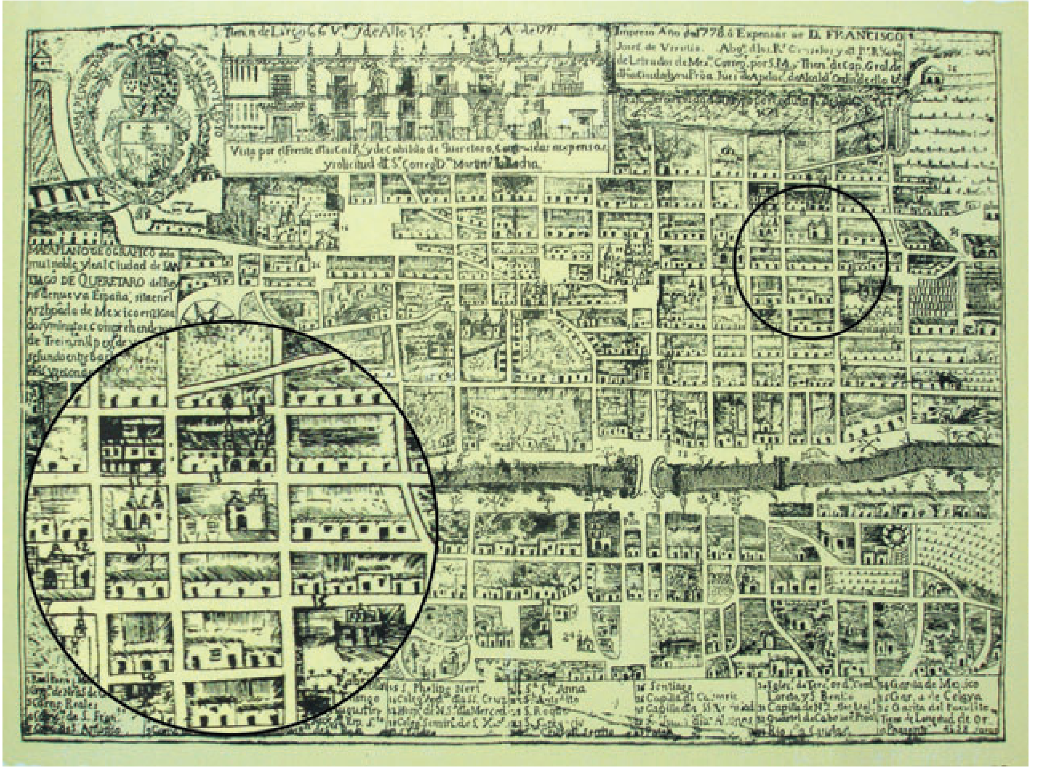

Figure 1 *Map of Queretaro city dated 1778, where the El Museo del Calendario building can be seen. The inset is an amplification of the region encircled on the map, and shows the position of the building in the city context.*

X-ray diffraction (XRD)

The X-ray diffraction patterns of the stucco powders were obtained using a diffractometer (Siemens D5000, Germany), operated at 35 kV accelerating voltage and a 15 A current, using a Cu Kα radiation wavelength of 1.5406 Å. The measurements were made at room temperature at a range of 10 to 70° in 2θ with a step size of 0.05°. Preparation of each sample consisted of grinding it to obtain a fine powder which was then passed through a grade 60 sieve.

Fourier transform infrared (FTIR)

IR spectra were obtained using a spectrophotometer (Bruker vector 33, USA) employing the diffuse reflectance technique with a resolution of 4 cm^{-1}. The sample preparation process consisted of grinding the sample to obtain fine stucco powder which was then mixed with KBr powder.

Scanning electron microscopy (SEM)

The microstructure and morphology of mineral constituents in the stuccos were recorded with a scanning electron microscope (Jeol JSM 5600, Japan) using secondary electrons to build the

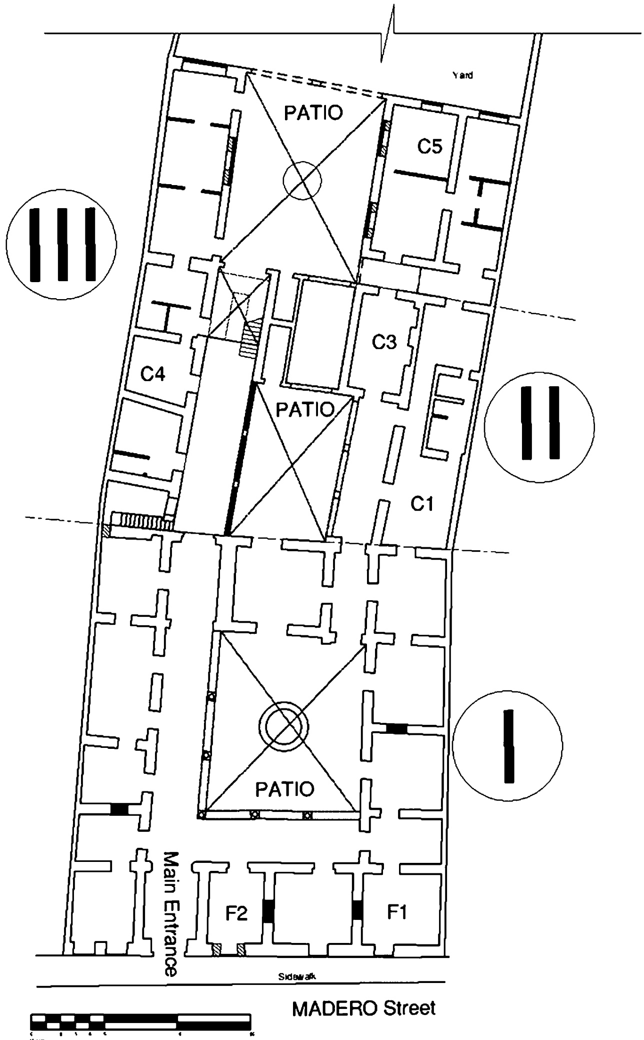

Figure 2 *Layout of El Museo del Calendario. The rooms where samples of different stuccos were taken are indicated.*

images. The microscope was operated at 20 kV accelerating voltage. Sample preparation consisted of application of a superficial gold film by sputtering to prevent electrostatic charge.

RESULTS AND DISCUSSION

XRD

Figure 5 shows the X-ray diffraction patterns of the stucco samples from the three different building stages. In all the samples the same constituents were detected. However, of these samples only three were chosen as part of the investigation. The crystalline structures found in sample F1 (stage I), correspond to quartz (SiO_2), albite [$Na(AlSi_3O_8)$], and calcite ($CaCO_3$),

Figure 3 *Photograph of the frontage of El Museo del Calendario, showing the conservation state before the restoration process.*

Figure 4 *Photograph of the building interior. Some temples in the old Colonial town of Querétaro can be seen. Those buildings are some of the monuments declared World Heritage sites by UNESCO in 1996.*

identified according to the International Centre for Diffraction Data Cards 03-065-0466, 01-071-1150, and 00-0050586, respectively. The presence of quartz was evidence of the use of sand in the formulation of the original stucco; albite makes known the use of pozzolan. Calcite was found instead of $Ca(OH)_2$ which is indicative of the prior use and later chemical transformation of the lime. In the X-ray pattern of sample C1 (corresponding to stage II), quartz (SiO_2), albite [$Na(AlSi_3O_8)$], and calcite ($CaCO_3$) were found. Once again the use of sand, pozzolan and lime were confirmed. Sample C4 from stage III exhibits the presence of the same compounds as those of C1. $Ca(OH)_2$ was not found in any of the samples because of the continuous interaction between lime and CO_2 in the environment, which produces $CaCO_3$ via the carbonation processes (Galván-Ruiz *et al.* 2007).

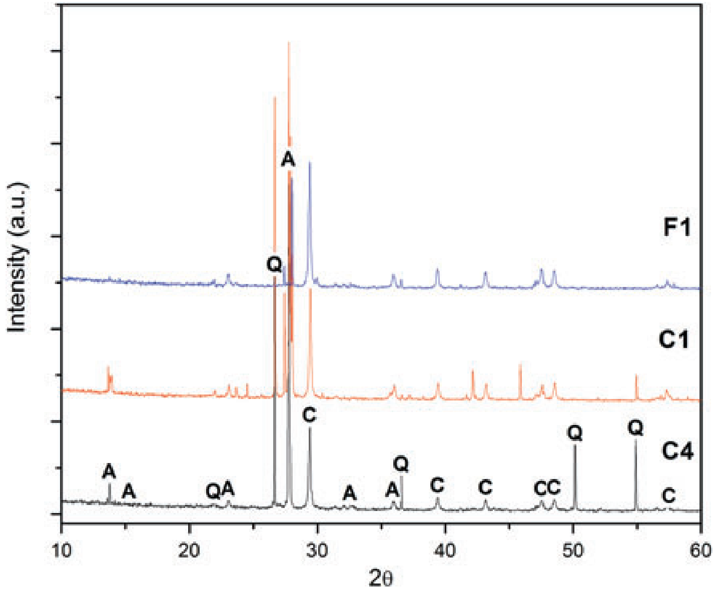

Figure 5 *X-Ray diffraction patterns of samples C1, C4 and F1. The main constituents were identified as albite (A), calcite (C) and quartz (Q).*

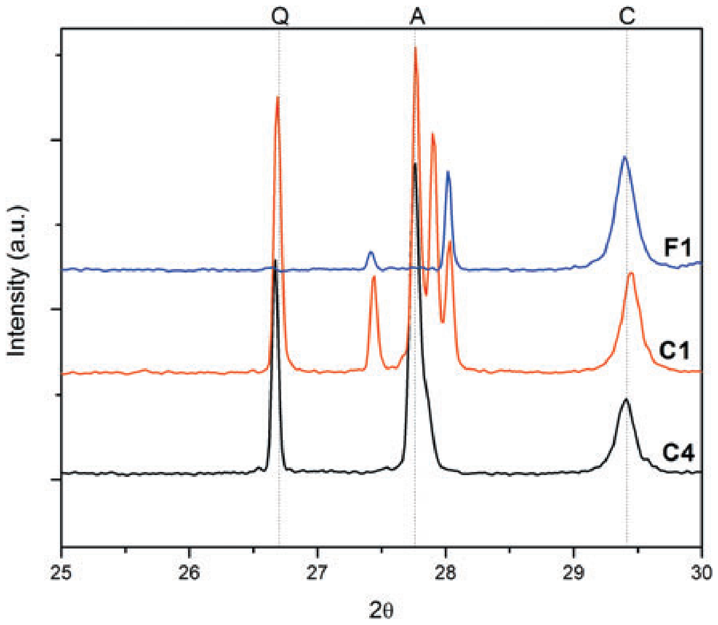

Figure 6 *Amplified 2θ regions show details of the signals from quartz (Q), albite (A) and calcite (C), allowing a comparison of relative intensities.*

The amplifications in the diffractograms in the range from 25° to 30° in 2θ, show in detail the peaks at 26.68, 27.78 and 29.4° which correspond to the largest intensity signals of quartz, albite and calcite, respectively (Fig. 6). The relative intensities of those signals are related to their corresponding concentration in the stuccos. By comparing the intensities it is possible to

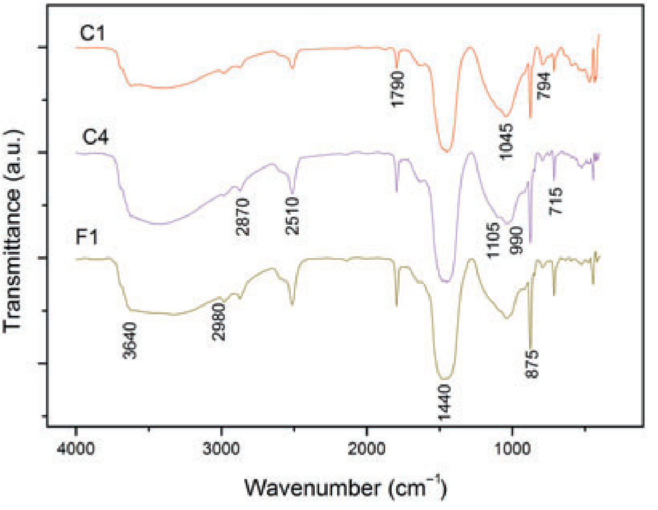

Figure 7 *FTIR spectra from samples C1, C4 and F1. The main bands are labelled and related to their corresponding mineral component in the text.*

establish that the samples are rich in sand and pozzolan in relation to the calcite content. The signals at 27.4, 27.9 and 28° correspond only to albite.

It is worth mentioning that a ratio among relative intensities could not be directly used to obtain the exact chemical composition of the stucco since the intensity of a signal in X-ray diffraction is a function that depends on different variables and one of them is concentration. In spite of this, comparison of the relative intensities could be useful in figuring out the approximate concentration of the different components in the stuccos.

A few small differences can be also observed in Figure 6; the most evident is the presence of three signals corresponding to albite in sample C1 and just one of these signals in F1 and C4 samples. This could be because the albite in C1 had a random crystal growth, whereas in F1 and C4 albite had crystal structures with preferential orientations. In addition, the quartz content in F1 is less than that in C1 and C4, but the presence of the mineral in F1 was confirmed in Figure 5.

Comparing the patterns seen in Figure 5 it is feasible to suggest that this building had in fact at least three different constructive stages, which also means that three different kinds of stucco were used. Taking into account the results shown in Figures 5 and 6, the main components in the stuccos are: sand, lime and pozzolan. Nevertheless, it is possible that other non-crystalline materials could be present.

FTIR

In spite of the fact that FTIR is usually employed to analyse organic compounds, this technique is also useful for characterizing inorganic substances. A qualitative analysis from the characteristic frequencies provides information to identify chemical constituents in a compound. Infrared spectra narrow down the options to a few specific components, if only one or two are present. In addition, a correlation of FTIR and XRD may be very helpful. Figure 7 shows the FTIR spectra from samples F1, C1 and C4. The wide band at 3640 cm^{-1} corresponds to O–H group matching with the presence of water in the samples. The wide form of this band implies that O–H groups must be forming hydrogen bridges. The bands at 1440, 875 and 715 cm^{-1} correspond to the three different elongation modes of C–O bonds while the bands at 2510 and 794 cm^{-1} are the harmonic vibration of some of those elongation modes. The minor bands at 2870 cm^{-1} and the first overtone at 2980 cm^{-1} correspond to the C–O group from the carbonate ion. The thin and intense band at 1790 cm^{-1} is also associated with the carbonate C–O bond. All these bands allow for the identification of $CaCO_3$.

The intense and wide bands at 1105, 1045 and 1018 cm^{-1} which are overlapped, relate to SiO_2 (quartz), which is the main component of sand. The presence of quartz was also confirmed by XRD analysis. The main bands corresponding to albite (1005, 1034 and 1150 cm^{-1}) are overlapped with the bands generated by quartz. The identification of albite using IR was questionable, but possible. The results from XRD confirm the identification of albite.

In FTIR, the intensity of the signals or bands could be directly associated with the concentration of a component in the sample. In fact, this correlation makes it possible to use FTIR as a quantitative analysis technique. But in this case, the overlaps between the quartz and albite signals make it difficult to use this information to determine the concentration of each component in the stucco. However, if a semi-quantitative chemical composition determination is carried out using calcite and quartz standards and the bands at 1440 and 1045 cm^{-1}, corresponding to main IR signals of calcite and quartz respectively, it is possible to obtain an average chemical composition ratio between calcite and quartz (lime:sand) from most of the original stucco samples. The average composition ratio was 2:1, which coincides with X-ray diffraction results.

SEM

The observations made using SEM show a superficial layer made of fine powders mainly of $CaCO_3$ in the samples, see Figures 8 (a) to 8 (c). This layer is the external surface of the stuccos. Below these fine powders, there is a solid bulk made of large particles which has low porosity and does not show cracks or fractures. Most of the boundaries observed among the large particles appear to have good adhesion. The chemical composition of the large particles showed a higher content of silicon and aluminium than that of the fine powders, according to energy dispersive spectrometry (EDS) analysis. The latter results indicate that albite and quartz are the main components of large particles and calcite appears to be more abundant in the small particles. These results also confirm the presence of quartz, albite and lime in the original stuccos. The solid appearances of large particles lead to the assumption that this material could be mechanically resistant. Figure 8 (a) corresponds to C1. The large particles seem to be attached through fine powders as if they were bricks in a wall. Amplification of the fine powders makes it possible to observe a flake-like morphology with well-defined edges, typical of $CaCO_3$. Similar morphologies were observed in Figures 8 (b) and 8 (c), which correspond to samples C4 and F1, respectively. The large particles show more defined edges in samples C4 and F1 and they possess a similar appearance to that of ceramic materials.

Reproduction of the original materials

Using the results from X-ray diffraction and FTIR listed above and the historical information about the composition frequently used in stuccos and mortars, different new stuccos were obtained varying the lime:sand:pozzolan composition ratio. In addition, those different materials were tested *in situ* in the building. Adhesion to the wall, hardness and workability were evaluated in the new stuccos. According to that evaluation, the best formulation found

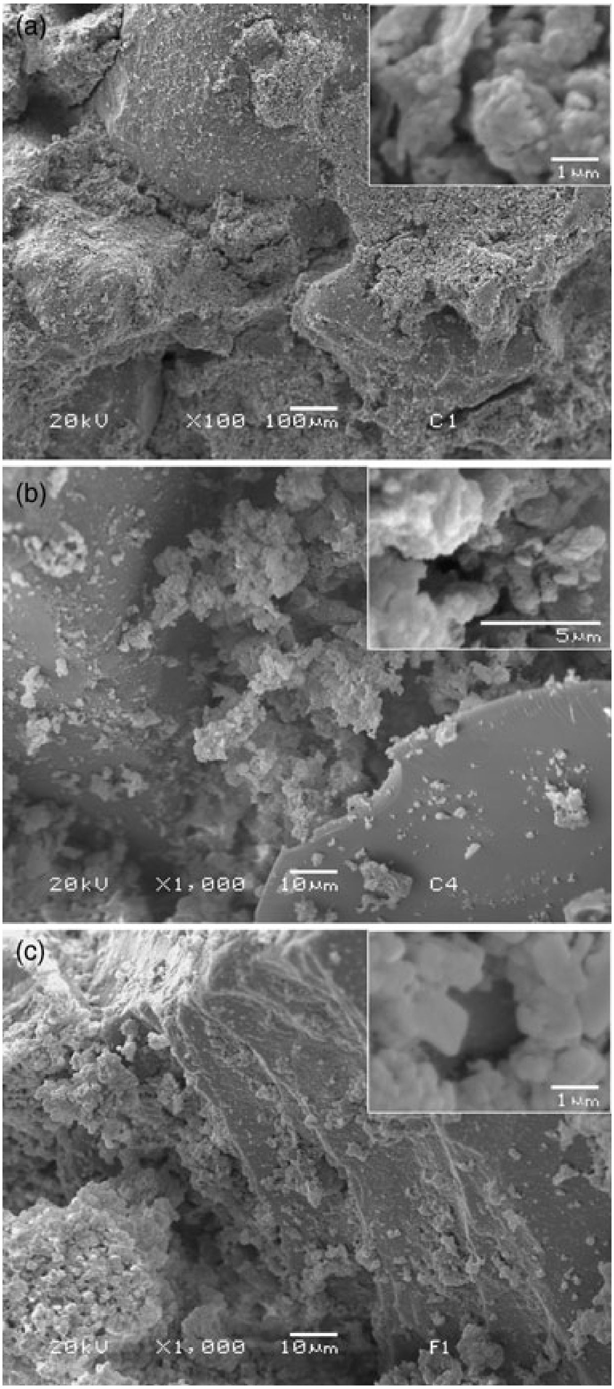

Figure 8 *Scanning electron micrographs of stuccos from different building stages. The images correspond to samples (a) C1, (b) C4 and (c) F1.*

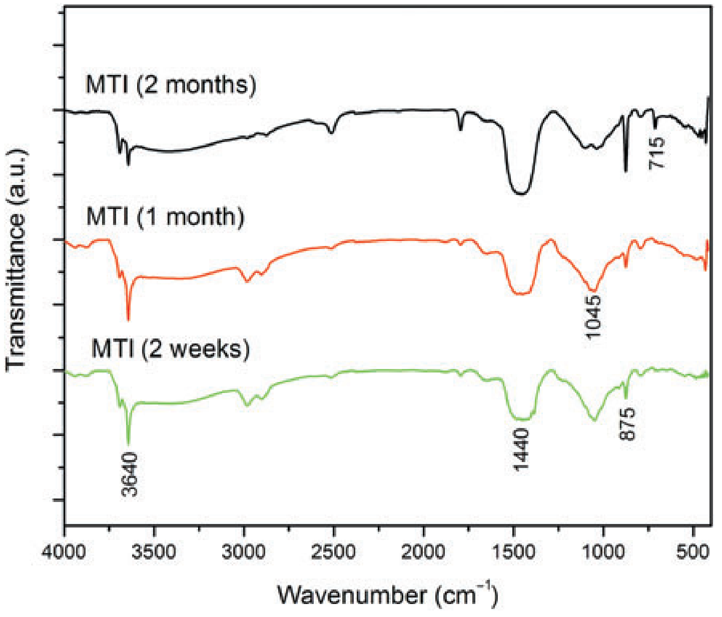

Figure 9 *FTIR spectra from new stuccos at different ages. The main signals are labelled to relate to their corresponding mineral components (see text). Notice the relative intensities of the main peaks of calcite and quartz.*

was selected which characterizes the analysis that is presented herein. Figure 9 shows FTIR spectra from a new stucco sample at different ages. It is possible to observe how the $Ca(OH)_2$ was gradually transformed to $CaCO_3$. The band at 3640 cm^{-1} corresponding to the O–H group was decreasing its intensity as a function of time. On the other hand, the intensity of the bands at 1440, 875 and 715 cm^{-1}, related to the carbonate group, increased over time. The band at 1045 cm^{-1} related to quartz (sand) maintained its intensity. If a comparison is made between Figures 7 and 9, it is possible to see that the new stucco aged 2 months is quite similar to those originally taken from El Museo del Calendario.

In a similar way, X-ray diffraction of the new stuccos shows several signals corresponding to portlandite (P) and others related to calcite (C). As times passes, the peaks of portlandite gradually decrease in intensity (see Fig. 10 middle and bottom diffractograms). In contrast, the calcite reflections increase in intensity in relation to time. The signals corresponding to quartz (Q) and albite (A) maintained their intensity through time. Some slight changes in those peaks can be observed in Figure 10, this apparent intensity variation is produced by the corresponding change in the relative intensities of the peaks from C and P, since these peaks are the most intense in the diffractograms, and the relative intensities for all signals are normalized compared to the large ones. Once again, if a comparison is made between the diffractogram of an original stucco (Fig. 10, top) and that corresponding to the 2-month-old 'newer' stucco (Fig. 10, middle), several similar signals can be found, and this fact supports the suggestion that the new stuccos have a similar chemical composition to the original ones.

Finally, the new stucco samples were observed in the SEM and several morphological similarities with the original stuccos were revealed. In the new stuccos a superficial layer made of small particles was observed, comprised of Ca, O and C. It is then possible to determine that the small particles are formed of portlandite and calcite, as shown by FTIR and X-ray diffraction

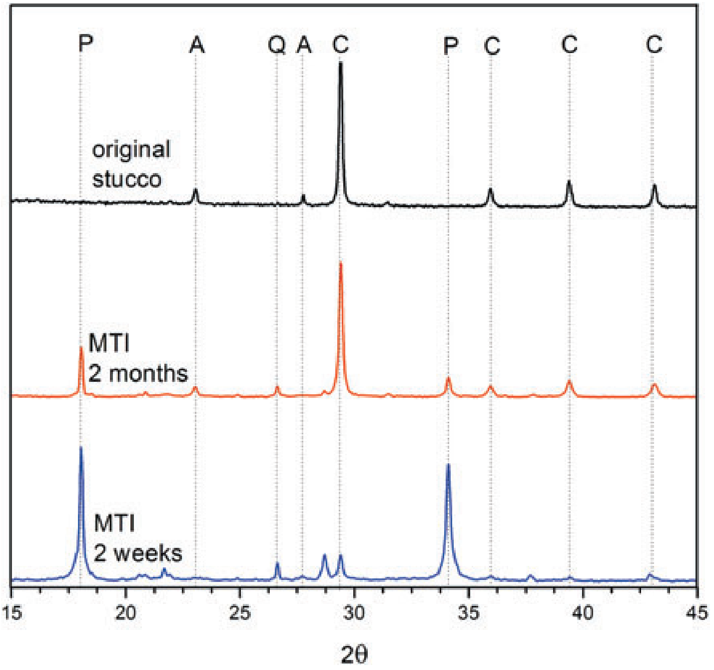

Figure 10 *X-Ray diffraction patterns from new stuccos at different ages. Identification of the signals is shown: P, portlandite; C, calcite; Q, quartz; A, albite.*

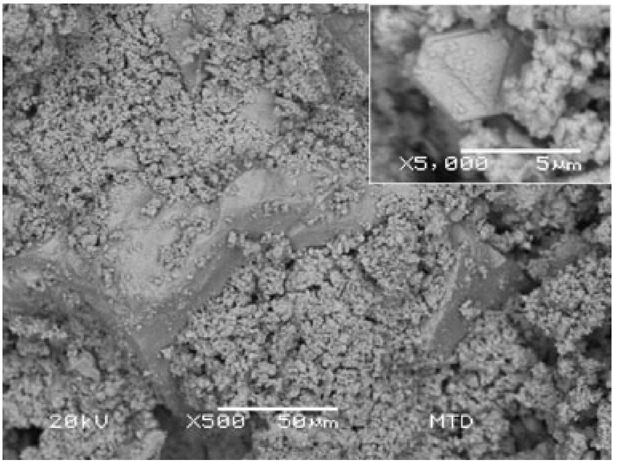

Figure 11 *Micrographs of new stuccos showing morphology and microstructure of small and large particles. The inset shows the detailed morphology and crystal growth habits of a large particle with well-defined edges and shape.*

results discussed above. A solid bulk found beneath these fine powders was made up of large particles consisting of Si and Al, quartz and albite (Fig. 11). The chemical composition of the superficial layer and the bulk was determined by use of EDS. The portlandite is still present in the new stuccos and it will undergo a chemical transformation to produce calcite as was previously mentioned. If Figures 8 and 11 are compared, a number of comparable microstructural and morphological characteristics can be found between the new and original stuccos. The large particles have well-defined edges, which are evidence confirming the crystal growth. In addition, the large particles have low porosity, and cracks or fractures were not observed. The morphology of small particles in new stuccos could be a little different from that found in the original materials. This morphological discrepancy is due to the presence of portlandite crystal, but this difference will disappear with the passing of time when most of the portlandite turns into calcite. In general, it is possible to assert that the microstructure and morphology of ancient and new stuccos are quite similar; consequently the macroscopic appearance will also be very similar.

CONCLUSIONS

According to the aforementioned results, it is possible to ascertain that the stuccos used during the different building stages of El Museo del Calendario have a similar chemical composition, which is mostly calcite, quartz and siliceous-aluminates. The siliceous-aluminate compounds were formed from the chemical interaction of lime and pozzolans. These compounds confirm the use of pozzolans in the formulation of original stuccos. The inorganic phase has a chemical composition ratio of lime:sand:pozzolan 2:1:0.5. The characterization procedure permitted the present investigators to determine not only the approximate chemical composition of ancient stuccos, but also their microstructure and morphology, which are necessary in order to reproduce them with similar appearance, performance and adhesion as the original products and restore the damaged stuccos. The reproduction of ancient materials through the use of the materials characterization process as presented herein was very successful. The chemical composition, microstructure and morphology of new stuccos are almost the same as those in ancient stuccos. In this respect it is possible to expect that the mechanical properties are also quite alike. This likeness between original and new materials, as well as a suitable technique of application of new stuccos, will prevent secondary effects in the original materials and possible segregations and degradation.

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