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Chemical and physical characterization of the stucco mihrab of the mausoleum of Muhammad Al-Hasawati, Fatimid period, Cairo, Egypt

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Abstract

Stucco mihrabs in Islamic buildings in Egypt are suffering from many causes of deterioration, mainly groundwater and salt weathering, which have caused the complete loss of the decorations of some of these mihrabs. Some other mihrabs need restoration and conservation, so a solution for this problem has become urgent. A physiochemical study using analytical techniques such as X-ray diffraction, X-ray fluorescence, Fourier transform infrared and scanning electron microscopy was done. This characterization study, on one hand made reproduction of the original material possible; on the other hand, the deterioration factors of the stucco were determined. All analytical methods indicated that the Al-Hasawaty stucco mihrab contains lime, gypsum, dolomite, quartz, anhydrite and bassanite; they also proved that sodium chloride (halite) is the principal salt causing deterioration.

Key words: stucco; mihrab; gypsum; lime; deterioration; conservation.

Introduction

The mausoleum of Muhammad Al-Hasawati (519-550 A.H. / 1125-1150 A.D.), is a small mausoleum that lies about 60 yards south-west of the mausoleum of Imam ash-Shafi. It is constructed of brick and coated with stucco, (Figure1). The stucco mihrab of the mausoleum bears the closest possible relationship to that of Sayyida Ruqayya, and is only very slightly exceeded by the latter in size and richness of decoration. It has the same fluted conch with a

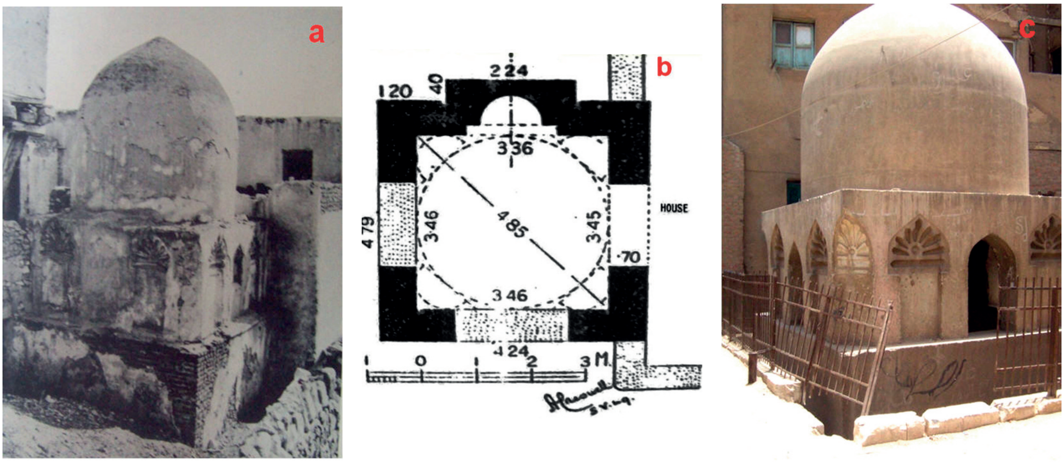

Figure 1. a) Al-Hasawati mausoleum before restoration (Creswell, 1952); b) the plan of Al-Hasawati mausoleum, scale 1:100 (Creswell, 1952); c) up to date picture of the mausoleum.

large medallion in the center, a triple scalloped edge, the same almost keel-arched outline, the same traces of bosses in the spandrels, a band of the same kind of plaited Kufic script on a shallow cavetto; the ribs of the conch are decorated with a simple guilloche and alternate arabesque, except for the bottom rib which is decorated with a band of erect and inverted triangles, the center of the vertical ones being occupied by a trefoil (See Figure 2) (Creswell, 1952).

The mihrab was deteriorating due to factors, mainly groundwater and salt weathering, which has caused the loss of some parts of the stucco motives, as well as depositing thick layers of salt (see Figure 2 a,b). As indicated in the literature, soluble salts are considered to be among the most important causes of decay. Salts cause damage by the growth of salt crystals within the pores, which can generate stresses that are sufficient to overcome the tensile strength of the material and turn it to powder (Doehne and Price, 2010). That was confirmed by Abd El Hady (1994) who said that soluble salts are very harmful to building materials as they have the ability to exist in different states of hydration. The crystallization of these salts within the pores takes place if the saline solution is between the state of saturation and supersaturation. Salts such as sodium chloride and calcium sulphates ($CaSO_4$ and $CaSO_4{\cdot}2H_2O$) cause serious damage to building material because the change from one hydrated phase to another is commonly associated with a volume change which in turns gives rise to forces on the walls of the individual pores (Abd El Hady, 1994).

Besides, the mihrab was suffering from large cracks related to substrate movement. According to Ashurst (1983), most of the aspects of the deterioration of stucco monuments relate to the deterioration of the building materials used in the wall more than to the stucco itself (Ashurst, 1983). For example, the support may be too weak to resist weathering for any length of time, this is the case of unbaked brick walls when the bricks are of poor quality and contain salts (Mora et al., 1984); water-soluble salts from bricks and mortar may dissolve under the influence of moisture in the structure. If salts do not migrate to the surface as efflorescence and accumulate behind an impervious surface coat, deterioration with damage of the structure will follow (Engelbrektsso, 1988). The heterogeneity of wall materials, differing both in porosity and thermal conductivity, may cause some areas to become zones of condensation, which is revealed by the appearance of clear or dark staining (Mora et al., 1984). Movement in the substrate may cause the bonding failure and cracking of plaster or stucco

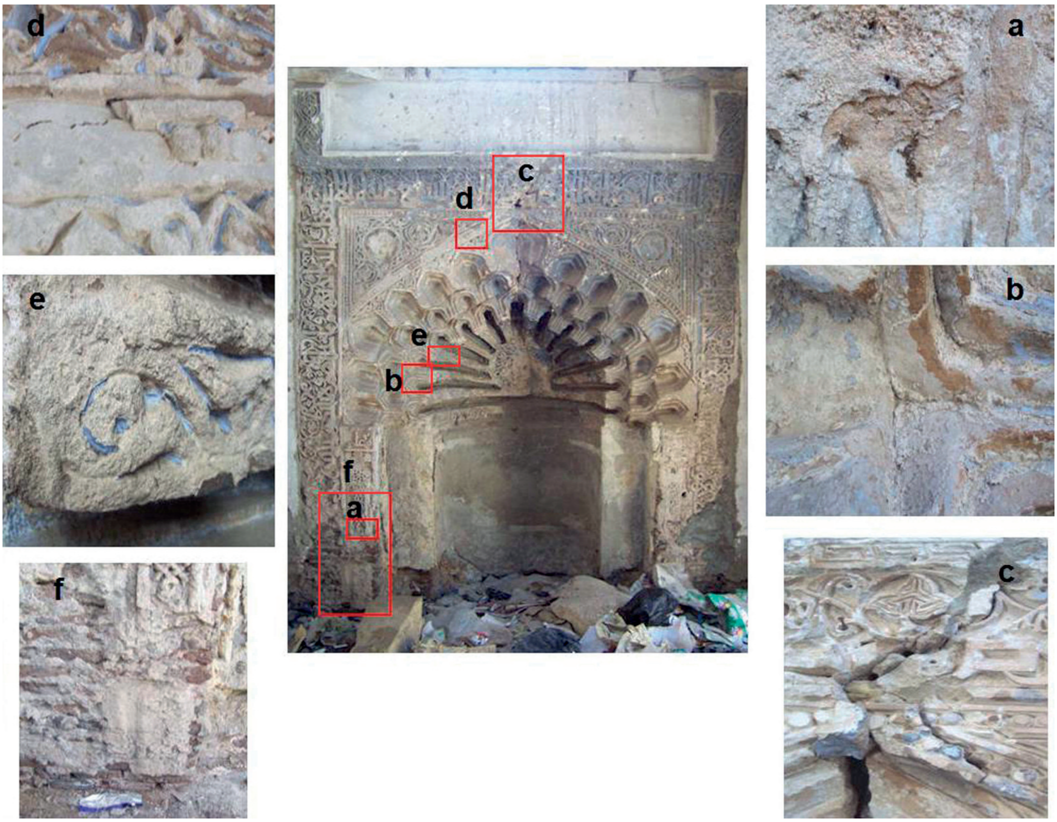

Figure 2. Deterioration aspects of stucco mihrab in Al-Hasawati mausoleum; a,b) thick layers of salt which deteriorated many parts in the mihrab; c) big crack at the top of the mihrab which may be related to the substrate movement; d) scaling of stucco layers which may be a result of bad application of stucco layers; e,f) etching and loss of some parts of stucco material at the bottom of the mihrab that may be a result of the severe effect of moisture and salt solutions.

(Elert and Rodriguez, 2002) (Figure 2 c,d).

In addition, there is scaling in the stucco layers of the mihrab, this aspect is related to a bad choice of stucco components, such as using an excess of binding material creating a risk of large cracks forming as the aggregate sets, which sooner or later causes detachment of the rendering from the support. Insufficient binding material, on the other hand, results in a lack of cohesion and in disintegration by powdering (Mora et al., 1984). Late hydration of the magnesium oxide in dolomitic lime might result in poor soundness; on the other hand, exposure to air pollutants such as sulfur dioxide might cause the formation of highly soluble, damaging magnesium sulphates (Elert and Rodriguez, 2002). Sometimes, scaling and etching of stucco motives are related to the bad preparation of the stucco layer, such as poor bonding, little or no key on substrate, high drying shrinkage of the backing coat, application of a strong coat onto a weak coat or substrate, application of a stucco or plaster layer over paint/whitewash/bitumen/ loose friable material, finishing too early on cement backing coats that are still too wet, etc. (Aitkenhead, 1995) (see Figure 2d).

Finally, the weakening of the stucco layer of the mihrab may be a result of the phase conversion of the gypsum component of the stucco layer, as gypsum is sensitive to excessive dryness. In effect, the gypsum can, at a temperature above 30 ^{o}C and a moderate R.H. (30 - 40%), gradually lose its water of crystallization to become anhydrite, thus weakening the rendering or stucco (Mora et al., 1984).The transformation of gypsum to anhydrite may be done directly or through intermediate steps forming bassanite and γ-anhydrite (Mori, 1986; Carbone et al., 2008; Ballirano and Melis, 2009; Milsch et al., 2011).

After displaying the deterioration of Al-Hasawati mausoleum stucco mihrab and the possible causes of deterioration, considering its restoration and conservation becomes more urgent. The appropriate stucco restoration requires three key components: the first is studying its composition, this implies identification of crystalline phases and definition of elemental composition and of mechanical properties; the second is related to the technology to be employed in reproducing the material to be used in the restoration process; finally there is the reproduction and development of techniques for applying stuccos and mortars (Galván-Ruiz, et al., 2009).

With this in mind, this article focuses on the study of the ancient stuccos of the case study in order to understand their composition and the causes of degradation, which will help in restoration, completion and strengthening of stucco motives.

Materials and methods

Sampling

Seventeen representative samples were collected carefully, using a micro-scalpel, to identify the constituents and degree of deterioration of the stucco mihrab. All the analyzed and investigated samples were carefully collected from areas without aesthetic value or from severely damaged parts (Table 1).

Table 1. Description of the stucco and salt samples collected from the stucco mihrab of the mausoleum of Muhammad Al-Hasawati investigated in this work.

Sample	Description
XR1, XR2, XR3	samples from areas with good state of conservation to represent the mineralogical composition of stucco material of the mihrab
Sd	a part of the white paint layer
Se	a part of the red brick joints
1a, 2a	red brick substrate samples (taken from deteriorated areas at the bottom of the mihrab)
Sa, Sb, Sc	salt samples were collected from different parts of the stucco mihrab to identify them
4,5,6	Samples were collected from detached parts of the stucco material of the mihrab for XRF analysis
IR1, IR2	Samples were collected from detached parts of the stucco material of the mihrab for FTIR analysis
SEM 1	SEM sample was collected from deteriorated part of the mihrab
SEM 2	SEM sample was collected from deteriorated part of the mihrab from the big crack at the center of the mihrab

X-ray powder diffraction (XRPD)

The X-ray powder diffraction patterns of the stucco powders were obtained using a diffractometer (Philips PW 1840), operated at 40 kV and 25 mA, using CuKα radiation and a receiving slit of 0.2 mm. The measurements were made at room temperature. Preparation of each sample consisted of grinding it in the dry form, by using a mortar and pestle to obtain a fine powder.

X-ray Fluorescence (XRF)

Three stucco samples were analyzed by XRF to determine the chemical composition of the stucco samples. The apparatus used is a Philips PW1400. The investigated samples were prepared in the form of pellets, using a manual press under a 20 tons load, and were analyzed using a Rh-Kα *(rhodium)* radiation tube at 50 KV and 50 mA. The chlorine ion was analyzed by potentiometer titration.

The loss on ignition (LOI) of the samples was determined by igniting 1g of the sample in a weighted platinum crucible heated to 950 ºC in an electric furnace for 30 minutes (first time) and then for 15 minutes (second time). The crucible and samples were cooled for 10 minutes before each weighting, performed after heating and weighting were repeated until constancy of weight was observed.

Fourier transform infrared Spectroscopy (FTIR)

IR spectra were obtained using a FT-IR Thermo Nicolet 760. The resolution is of: 4 cm^1 (Region 4000 : 400 / Absolute threshold 0.002 / Sensitivity : 50). The sample preparation process consisted of grinding the sample to obtain fine stucco powder which was then mixed with KBr powder, with a sample/KBr ratio of 1:15. The FTIR quantitative analysis was done at the micro analytical center of Cairo University.

Scanning electron microscopy (SEM)

The microstructure and morphology of mineral constituting of the stuccos were analyzed with a scanning electron microscope FEI Quanta 200. The microscope operated at 30 kV accelerating voltage. Sample preparation consisted of application of a superficial gold film by sputtering to prevent electrostatic charge.

Results and discussion

X-ray powder diffraction (XRPD)

The XRPD patterns of the stucco samples from El-Hasawaty stucco mihrab (Figure 3) indicate the following results which are resumed in Table 2.

The semi-quantitative analysis of the mineralogical components indicates that calcite (35 wt.%) is one of the main components of the stucco samples as well as gypsum (ca. 20 wt.%). The results point out that the stucco mihrab of Al-Hasawaty was prepared by application of gauged stucco (gypsum lime stucco), (Figure 3). Phase quantification was estimated from the relative intensity of reference peaks of the mineral occurring within the mixtures.

After the overview of results we note that:

A) The content of quartz of XR 1 is very high; such a high content cannot be used in a stucco mix, as it will make the engraving of motives more difficult. This anomalous value may be related to poor mixing of stucco or to deterioration affecting the binding materials through dissolution and leaving sand. The quartz content of the three samples may be due to an intentional addition or may be considered a natural impurity in the raw materials (limestone and gypsum stone before calcination). The sand grains grading proved that there was a good preparation of raw materials, as all sand grains passed through a sieve of 150 microns.

B) The presence of β-anhydrite in the three samples with an average of about 6%, this ratio may be related to the following possibilities:

1) β-anhydrite may be a result of exposure to high temperature and relative humidity for a long

Table 2. The approximate XRD analysis results of three stucco samples from El- Hasawaty stucco mihrab.

Mineral	XR 1 (%)	XR 2 (%)	XR 3 (%)	Average of XR 2 and XR 3 (%)
Calcite	19	35	37	36
Gypsum	14	24	15.5	19.75
Quartz	35	18	12.5	15.25
Dolomite	9	15	10	12.5
Anhydrite	2.5	8	3.5	5.75
Bassanite	20.5	-	21.5	10.75

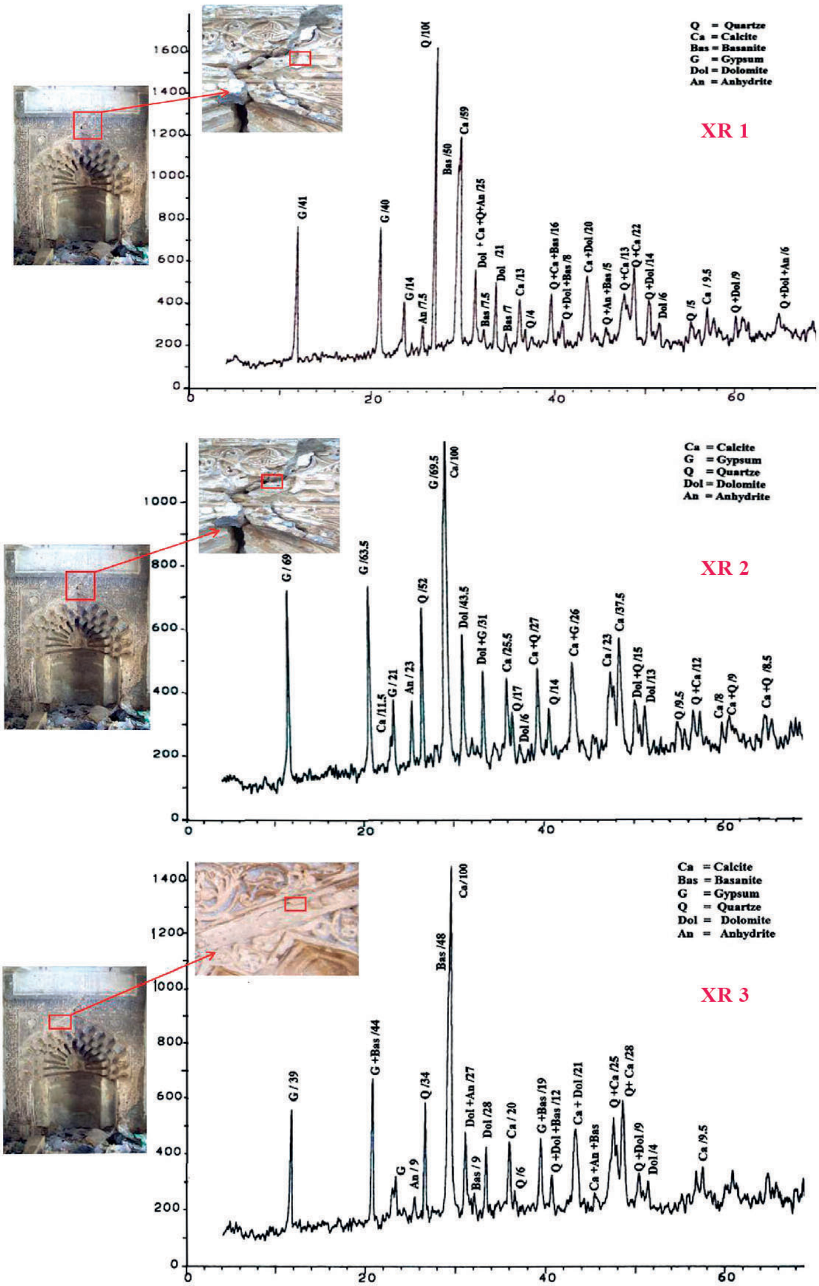

Figure 3. X-Ray diffraction patterns of archaeological stucco samples from El Hasawaty stucco mihrab used to reconstruct the archaeological stucco material, the results proved that the stucco material consists of calcite, gypsum, dolomite and sand (gauged stucco).

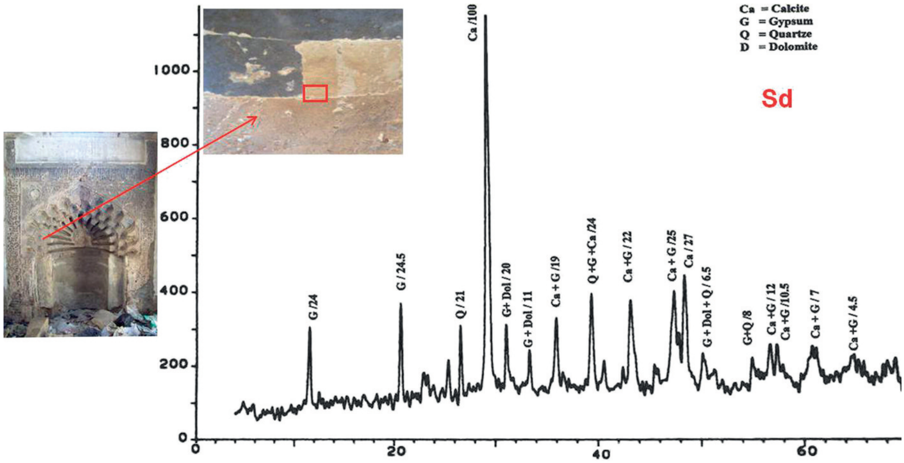

Figure 4. (Sd) X-Ray diffraction analysis results of the white layer of lime paint which proved that paint wash consists essentially of lime.

time (more than 800 years), according to Mora et al. (1984);

2) It may be an impurity related to the raw materials used as a source for gypsum and this material was not affected by the temperatures used for the calcination of gypsum;

3) β-anhydrite may have resulted from the overheating of gypsum raw materials during

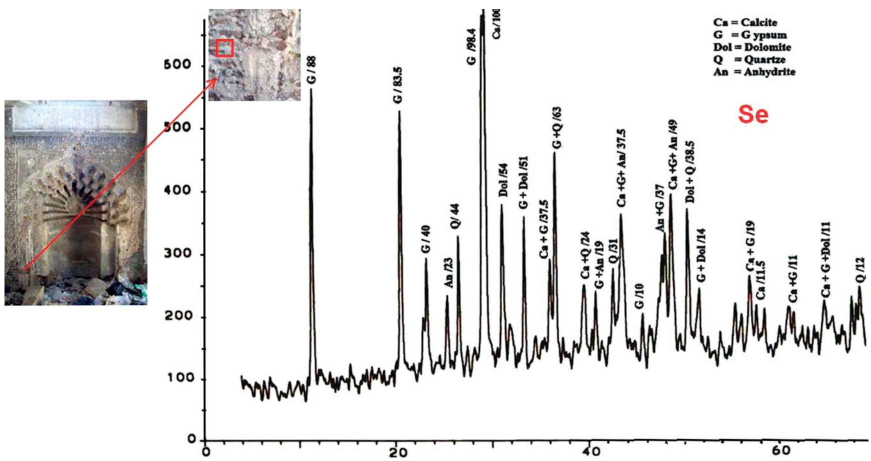

Figure 5. (Se) X-Ray diffraction analysis of the mortar used in red brick joints of El Hasawaty mausoleum which proved that the joints components resemble the results of stucco material of the mihrab, testifying the direct application of stucco material (mortar) and use of the semi-empty joints as keys for fixing the stucco layer.

calcination, according to Kamel (1986).

4) Anhydrite may be an intentional additive to accelerate setting but this may not be an acceptable reason as in some samples the ratios do not exceed 2%, (Marie, 1996).

C) The dolomite content (ca.12.5 wt.%) may be related to the use of dolomitic limestone (this kind of stone may have been carved from El-Giza plateau or the base of El-Moqattam Mountain, as it was characterized by dolomite crystals, according to Abd El Hady (1997).

D) The bassanite content which exceeded 20 wt.% in XR, 3 may be considered a sign of the active transformation from gypsum to bassanite which sometimes led to transformation to anhydrite (γ-anhydrite then to β-anhydrite) or may have resulted from the drying process of stucco samples before X-ray diffraction analysis, (Charola and Centeno, 2002). Also, gypsum ($CaSO_4 \bullet 2H_2O$) dehydrates to γ-anhydrite ($CaSO_4$) via an intermediate step forming hemihydrate (bassanite; $CaSO_4 \bullet 0.5H_2O$) first (Milsch et al., 2011). The conversion of bassanite to γ-anhydrite starts at 388 K and is completed at 408 K (Ballirano and Melis, 2009). Carbone found that gypsum dehydrates to γ-anhydrite in a single-step process without the occurrence of bassanite as an intermediate product (Carbone et al., 2008).

XRPD of the red brick used in the support proved that the red brick of the substrate contains quartz, orthoclase, hematite and magnetite. The high percentage of halite in the two samples explains the expected damage by this soluble salt, while the calcite in sample 1a may be a result from the stucco layer (Figure 6, 1a,2a).

XRPD of three selected salt samples from different parts of the mihrab proved that sodium chloride (halite) is the principal factor of deterioration, which may explain the thick layers of salt on most parts of the mihrab (Figure 7, Sa, Sb,Sc).

X-ray Fluorescence (XRF)

According to the results of the chemical analysis by XRF, the presence of SiO_2 is related to the occurrence to quartz (sand), CaO to calcium carbonate; the presence of CaO, SO_3 and SO_4^{-2} gives evidence of the occurrence of gypsum and that of Cl^{-}+Na_2O to sodium chloride. Finally, MgO and CaO testify the occurrence of dolomite, small amount of other oxides indicate that they are no more than impurities. The presence of Fe_2O_3 may make the transformation of the calcitic component of stucco to gypsum easier, as the oxidation of SO_2 to SO_3 occurs by catalytic action due to surface impurities, such as Fe_2O_3, colloidal deposits, to $CaCO_3$ itself, to Ca^{2+} SO_4^{2-} in solution, to the gypsum already formed, to humidity, and finally to sulfur oxidizing bacteria (Table 3) (Bahragov et al., 1999).

Fourier transform infrared (FTIR)

With the aid of Domenechet al. (1997) and Galva-Ruiz et al. (2009), the FTIR results of the two selected stucco samples as follows: calcite can be seen through stretching vibration v2 874 cm^{-1} and 1438 cm^{-1}; gypsum can be identified by the presence of absorption bands related to the stretching frequencies of O-H bond 3547 cm^{-1} and

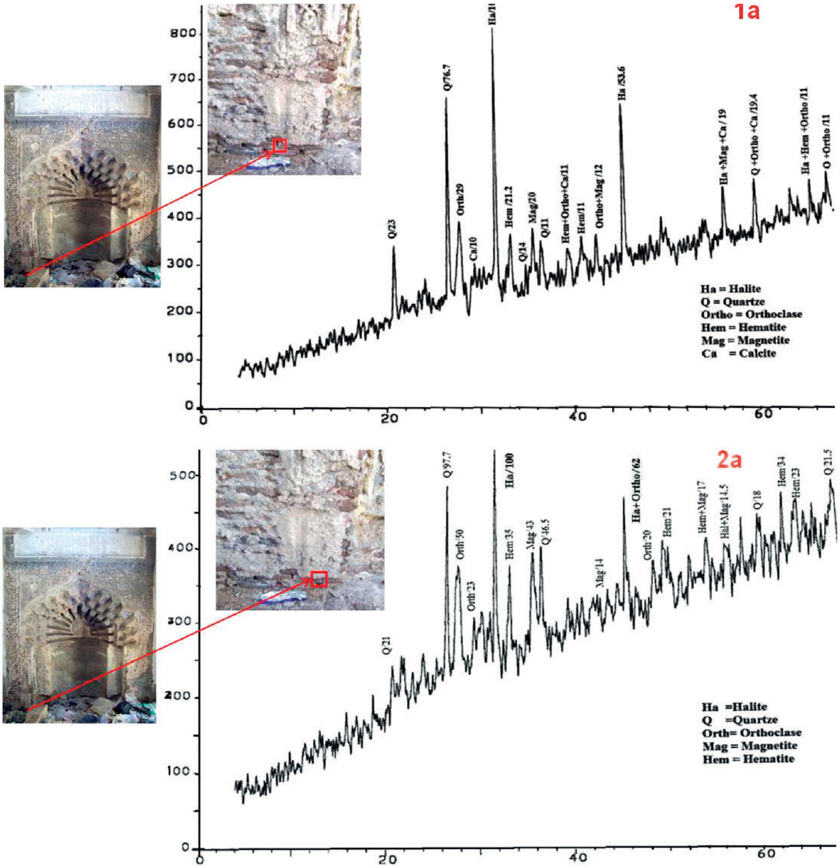

Figure 6, 1a, 2a. X-Ray diffraction analysis results of the red brick used in the support (the wall) proved that it consists of quartz, orthoclase, hematite and magnetite, while its main deterioration factor is sodium chloride (halite).

3406 cm^{-1} and from the deformation frequencies of O-H bond 1621.24 cm^{-1}. Absorption bands which concern calcium sulphate can be seen at v3 (1119 cm^{-1} and 1145 cm^{-1}), also at v4 (670 cm^{-1} and 903 cm^{-1}) (Figure 8).

Scanning electron microscopy (SEM)

The observations made by SEM of deteriorated stucco samples from the mihrab show the appearance of halite crystals (the salt was identified by XRPD) on both surface and in the depth, as well as the severe disintegration of the surface which may be related to the transportation of some mineralogical components by the effect of sodium chloride solutions (Figure 9, A,B).

Moreover, SEM shows the appearance of plant fiber parts (they resemble chopped straw). It may

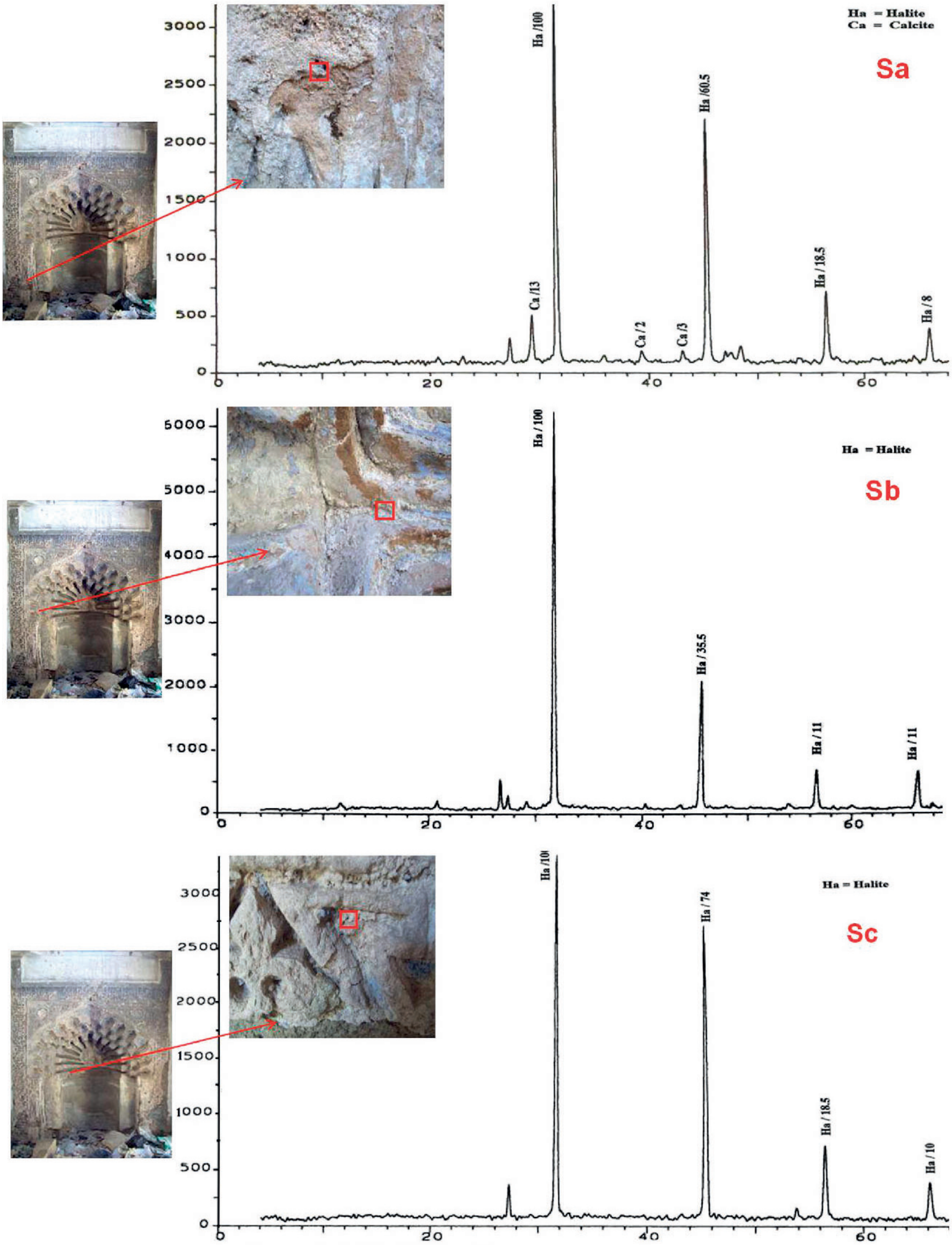

Figure 7. (Sa,Sb,Sc) X-Ray diffraction results of three selected samples of salt from different parts of the stucco mihrab proved that sodium chloride is the main deterioration salt of the mihrab.

Table 3. The results of X-ray Fluorescence analysis results of three stucco samples from Al- Hasawaty stucco niche. The results are confirming the results of X-Ray diffraction analysis results.

Oxides	Sample 4 (%)	Sample 5 (%)	Sample 6 (%)
SiO_2	1.35	1.52	1.48
Al_2O_3	0.41	0.41	0.40
Fe_2O_3	0.83	0.93	1.00
CaO	28.38	33.21	24.43
MgO	1.97	1.96	2.99
SO_3	30.86	36.07	25.42
Na_2O	17.76	4.14	22.98
K_2O	0.86	0.99	1.24
TiO_2	0.26	0.31	0.29
P_2O_5	0.48	0.61	0.74
L.O.I	16.59	19.73	18.78
Soluble Cl^{-}	14.38	12.49	17.02
Soluble SO_4^{2-}	18.67	24	16.4

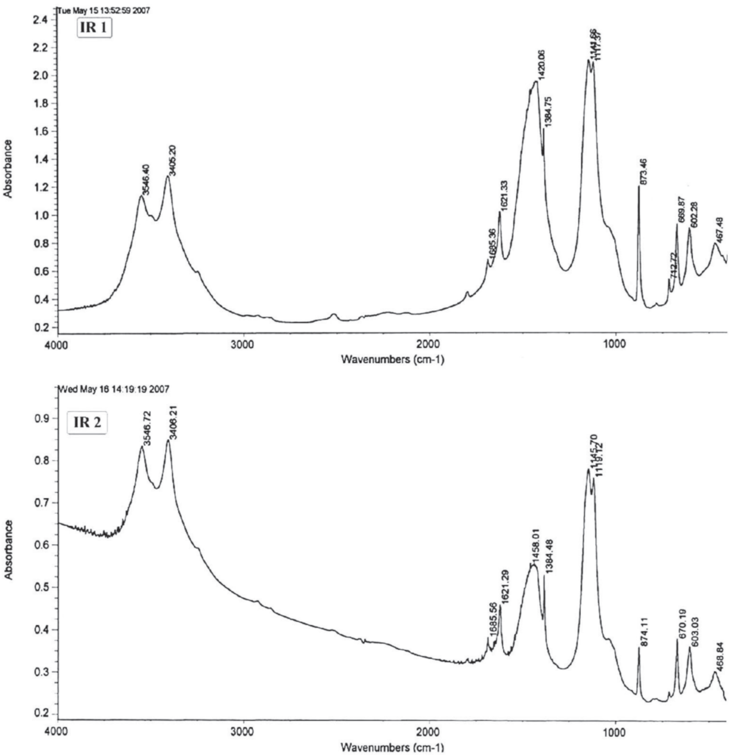

Figure 8. (IR1,IR2) Infrared spectra of two stucco samples from the mihrab confirmed the results of XRD and XRF analyzes.

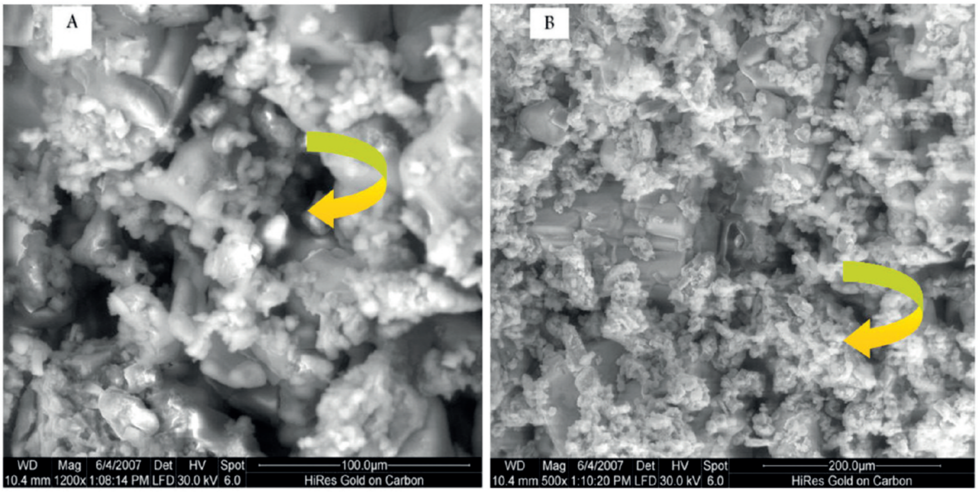

Figure 9, A,B. Scanning electron micrographs of deteriorated stucco samples from the mihrab show the bad effect of halite on the microstructure of the stucco samples.

be unlikely that these fibers should be used in mixing stucco that will be engraved, as it will make the process of engraving more difficult, in addition to the fibers being visible on the surface. The shape of the sample and its area on the mihrab may indicate that the sample was part of mortar improved by plant fibers and used to close a large crack seen at the center of the mihrab (Figure 10).

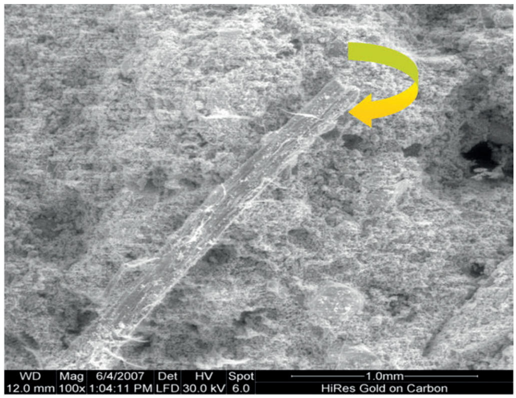

Figure 10. Scanning electron micrograph of stucco sample from the mihrab shows the used plant fibers in the stucco mix in the restoration of a big crack seen at the center of mihrab.

Conclusion

This work is part of the restoration and conservation project stucco mihrab of the El-Hasawaty mausoleum; as understanding of the mineralogical components of stucco is considered the main target that can help in reconstructing the stucco material, which is important for the completion of stucco motives and in knowing the deterioration factors by identifying aspects of the deterioration and determining acceptable procedures to abstract salts from stucco through identification of the kind of salt. The analytical methods used in this paper proved that El-Hasawaty stucco mihrab consists of calcite, gypsum, dolomite and quartz; in addition, halite is the main factor in the deterioration.

This conclusion shows that elimination of the source of salts is very urgent on one hand, and water (in a poultice) is the acceptable method for extracting the soluble salt (halite), on the other hand.

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