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Reconstructing the historic stucco mortars using XRD analysis and the calculation of the molecular weights of compounds

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Abstract:

Reconstruction of the historic stucco mortars is an important issue for its utilization in the restoration of historic stucco either for motives completion, edge pointing, crack filling or preparation of experimental samples. Analytical study by XRPD analysis and the calculation of the molecular weights of the binding materials of the intermediate phases (hemihydrate, anhydrite and portlandite) and the final phases of the historic stucco mortars (gypsum and calcite) was done to put a new methodology for the reconstructing of historic stucco mortars. The results of the study proved the similarity among the XRPD results of the historic stucco samples and the new reconstructed ones. That may justify its use as an approach for reducing the error in the reconstruction of the historic stucco mortars.

Keywords: Reconstruction; Stucco; mortar; XRPD; molecular weight; Fatimid mihrab.

1- Introduction

Reconstruction of stucco mortars is carried out to achieve two aims; the first aim is to prepare standard stucco samples which match the chemical and mineralogical composition of the archaeological stucco, these samples could be used for the evaluation of surface treatments. The second aim is to prepare a mortar for stucco motives completion, pointing mortars and cracks filling (Kamel, 2014).

Many researchers had studied the examinations and analyses used for mortars reconstruction. Some of them tried to set up methodologies for this target [(Berlucci & Ginanni Corradini, 1995), (Maravelaki-Kalaitzaki, et al., 2005), (Arıoglu & Acun, 2006), (Marques, et al., 2006), (Galvan-Ruiz, et al., 2009), (López-Arce , et al., 2010), (Maravelaki-Kalaitzaki, et al., 2010)].

Many researchers had proven that XRD analysis is one of the most important analyses which can be used as a helping tool in the reconstruction of historic stucco mortars, (Larsen ,2002), (Galvan-Ruiz, et al. 2009), (Kamel and Abo Elyamin, 2018), (Kamel,et al.2019).

The data acquisition of the integrated information to reconstruct stucco mortars is a difficult mission because of their complexity and diversity. Moreover, these procedures must ensure the physical, mechanical and chemical compatibility between the historic stucco mortars and the new proposed ones (Marques, et al. 2006).

Erlin and Hine (1987) noted that the skilled specialist is not only able to analyze the stucco mortars, but also to understand how deciphering the analytical data to obtain meaningful and fruitful information.

1.1. The role of XRD analysis in the reconstruction of the historic stucco mortars

XRD analysis is a vital method that has been widely used in the identification of stucco mortars. It gives direct information about the minerals because it deals with their crystalline structure (Helmi, 1994).

Galvan – Ruiz, et al.(2009) pointed that in spite of the intensity of a signal in X-ray diffraction is a function that depends on different variables and one of them is concentration, but the comparison of the relative intensities could be useful in figuring out the approximate concentration of the different minerals in the stuccos. Sanchez-Moral et al. (2005), Marques, et al. (2006) and Karatasios et al. (2007) had used X-ray diffraction for monitoring the conversion of portlandite (calcium hydroxide) to calcite (calcium carbonate).

Ashurst (1990) noted that the specification of stucco mortars cannot be built only on the simple chemical analysis, as there are many factors affect the condition and the performance of the stucco mortar such as the original water to binder ratio, the rate of drying out, the method of mixing, application methods and conditions of the aggregates.

Moreover, there are difficulties in identification of the constituents as the calcareous aggregates will be digested with the calcareous binder material in acid resulting in a misleading binder: aggregate proportion. Also, there is a problem in distinguishing the impurities of clay minerals and the silicates of hydraulic cements.

Furlan (1991) stated that the clear determination of the binding material content in the stucco mortar is very important in the reconstruction of the mortar used for the completion or replacement processes. While Lee and Larsen (2002) reported that ratios between gypsum and lime that are identified by analysis do not necessarily provide correct proportions of the stucco mortar reconstruction.

What was observed by Lee & Larsen motivated the researcher to contribute in reducing the error ratio in the results of XRD analysis of stucco mortars containing gypsum and lime. The author noted that most researchers depend on the approximate ratios of the resulting minerals such as calcite and gypsum while these minerals will not be used as binders as portlandite and hemihydrate will be used in the stucco mix as intermediate phases.

Here, there is an important question, how we can calculate the weight of the intermediate phases (portlandite, hemihydrate and anhydrite) - which will give the weight of the final phases of minerals detected in XRD analysis (calcite and gypsum) - after the complete reaction of hydration ?

The answer starting point had happened while studying the paper of Pique (1992) as he had studied gypsum by DTA-TG and concluded his study by this phrase "the entire weight loss is 20%which agrees with the values calculated by stoichiometry for the full reaction".

So, a question was raised why we cannot use the molecular weight of the compounds to reduce the XRD analysis error while reconstruction of gypsum and lime stucco mortars. As this method may help in determining how much weight of hemihydrate or calcium hydroxide will give the specified weight of gypsum and calcite after their hydration reaction. These results may be monitored by the XRD analysis.

For that, a methodology will be applied on archaeological stucco samples, and try to specify how much this methodology - cooperation between XRD analysis and the calculation of the molecular weight of the binding materials intermediate and final phases- can play a real role in optimizing the analysis results.

2. Materials and methods

Three representative samples were collected carefully by a micro scalpel from deteriorated and unseen parts from the main stucco mihrab of Sayyida Ruqqya mausoleum - an Islamic mausoleum was built in the Fatimid period, located at El-Ashraf street and near ibn Tulun Mosque, 527A.H. / A.D.1133- (Creswell, 1951), Figure 1 . These stucco samples were analyzed by XRPD analysis to identify the mineralogical composition using a diffractometer type Philips PW 1840, Netherlands, operated at 35 kV, using a Cu Ka radiation wavelength of 1.541874 Å. The reference database used for matching is a PDF-4 + 2015RDB. Also, the XRPD analysis was used to identify the mineralogical composition of the reconstructed stucco samples which will be compared with the results of the historic stucco samples.

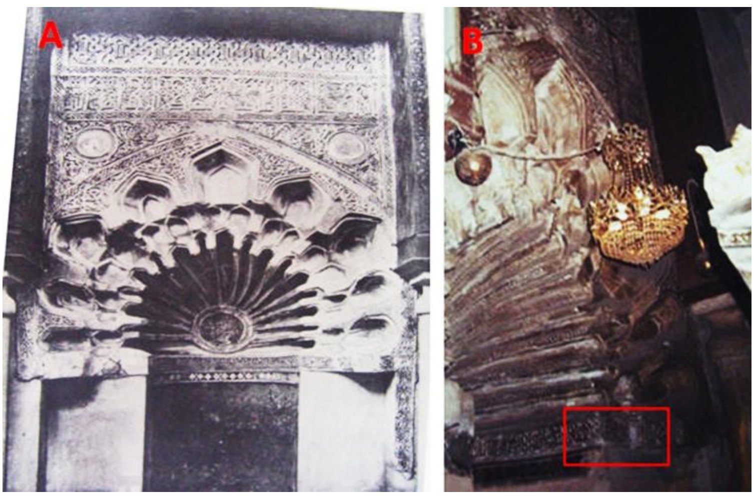

Figure 1 (A) The main stucco mihrab of Sayyida Ruqqya mausoleum (Creswell, 1951). (B) Sampling location.

2.1. Casting of the reconstructed stucco samples

After identification of the approximate mineralogical composition of the three historic stucco samples of the main stucco mihrab of Sayyida Ruqqya mausoleum by XRPD analysis; the proposed methodology was applied to identify the intermediate phases such as portlandite and hemihydrate. Then, the final mineralogical results were cast as a thin layer of mortar on a smoothed surface to enhance the carbonation of calcium hydroxide (slaked lime) to calcium carbonate (calcite). After three months, three samples of the cast layer were analyzed by XRPD analysis. Then, the results were compared with the results obtained from the historic stucco samples.

3. Results and discussion

The XRPD results of the analyzed stucco samples of the mihrab are resumed in table 1 and figure 2.

Table 1 The XRPD results of the analyzed three stucco samples of Sayyida Ruqqya main mihrab.

The Compound	S.(1m) %	S.(2m) %	S.(3m) %	Average ratio % of the compound in the three samples
Gypsum	71.2	56.1	59.4	62.23
Anhydrite	6.3	7.5	3.2	5.66
Basanite	2.7	4	2.5	3.06
Calcite	5.9	22.6	26.9	18.46
Portlandite	8.6	1.6	3.5	4.56
Quartz	5.4	8.2	4.5	6.03

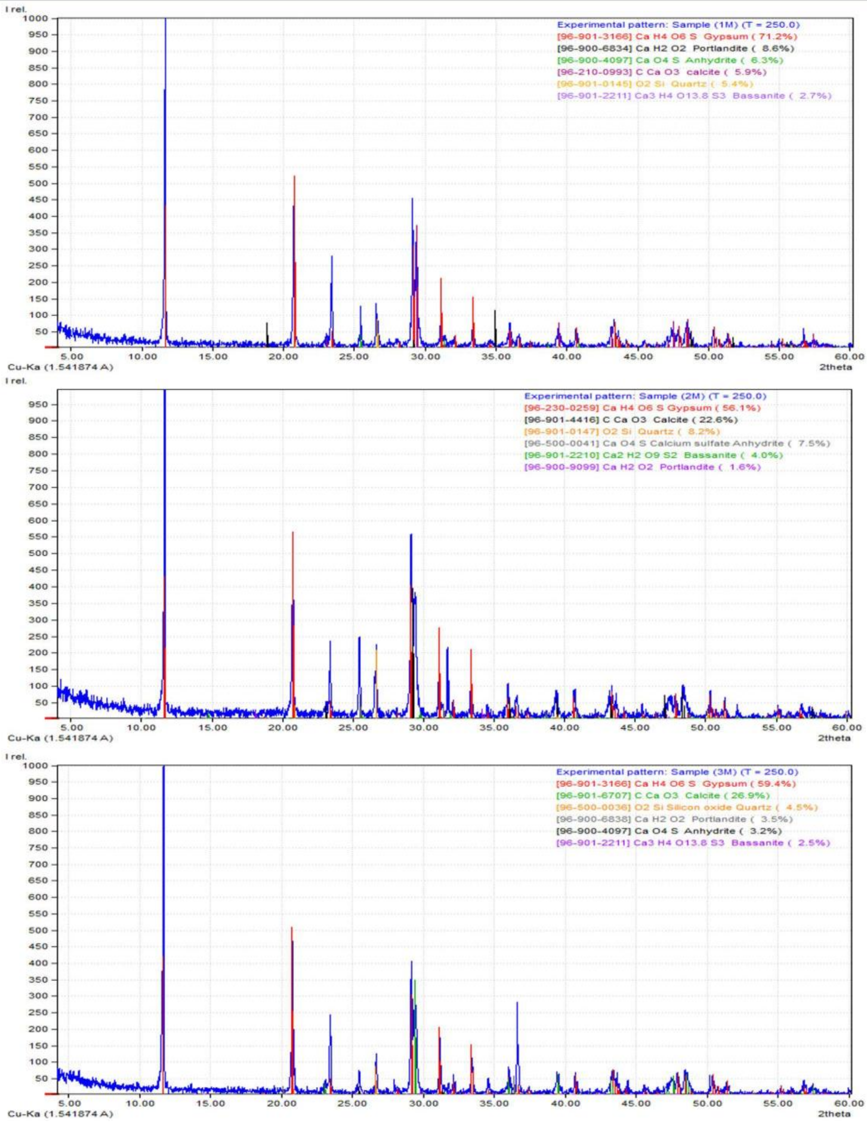

Figure 2 (1m, 2m and 3m) X-ray diffraction patterns of the analyzed three stucco samples of Sayyida Ruqqya main mihrab.

3.1. The practical procedures of the proposed methodology

While the reconstruction of historic stucco mortars, we cannot depend on the approximate ratios of the resulting minerals such as calcite and gypsum as these minerals will not be used as binders in the proposed stucco mix. So, we should convert these phases to the intermediate phases such as portlandite and hemihydrate .That conversion can be achieved through the calculation of the differences in molecular weights as will be clarified:

Gypsum ⟶ hemihydrate

$CaSO_4.2H_2O \longrightarrow CaSO_4.0.5\,H_2O$

$40+32+64+2(1\times2+16) \longrightarrow 40+32+64+ \frac{1}{2}(1\times2+16)$

$172 \longrightarrow 145$

So, the weight loss from gypsum phase to hemihydrate phase is about, 15.7% of the gypsum weight, but the weight increase related to the conversion of anhydrite to hemihydrate can be calculated as follows:

$CaSO_4 \longrightarrow CaSO_4.0.5\,H_2O$

$136 \longrightarrow 145$

So, the weight increase relates to the conversion of anhydrite to hemihydrate is about, 6.62% of the anhydrite weight.

The conversion of calcite to calcium hydroxide weight loss:

$CaCO_3 \longrightarrow Ca(OH)_2$

$40+12+48 \longrightarrow 40+34$

$100 \longrightarrow 74$

So, the weight loss of the conversion of calcite to calcium hydroxide (portlandite) is 26%.

The previous calculations of compounds molecular weight can help in identifying the approximate (the near real) ratios of the intermediate binding compounds (hemihydrate and calcium hydroxide), as clarified in Table 2:

The components which will be used in the stucco mix can be identified from the resulted approximate ratios of minerals as follow:

- The first binding material (hemihydrate) could be calculated through the summation of the results related to gypsum, bassanite and anhydrite. As these three phases are gypsum phases. So, hemihydrate ratio will be as follows: 52.46+ 5.666 + 3.26 = 61.386 ≈ 61.4 weight units.
- The second binding material (calcium hydroxide) could be calculated through the summation of the results relate to calcite and portlandite, as these two phases are calcite phases.

So calcium hydroxide ratio will be as follows: 13.666 + 4.566 = 18.232 ≈ 18.2 weight units.

- The ratio of quartz is fixed because it will be used as in its original form; 6.03≈ 6 weight units.

3.2. The comparison between the results of the reconstructed stucco samples and the historic samples results

The comparison of the XRPD results was carried out through the numerical results of the approximate results of the XRPD analyses as well as the resulted shape of charts as shown in table 3 and figures (2 and 3).

The XRPD results of the historic stucco samples of Sayyida Ruqqya main mihrab and the XRPD results of the reconstructed stucco samples proved the similarity of their final ratios of mineralogical compounds. In spite of the similarity of numerical results ratios between the two groups of samples, there are some differences in the shapes of their resulted charts. This may be related to the differences in the crystallinity of the resulted minerals phases and not to the differences in the chemical composition (Galvan-Ruiz, 2009).

The similarity of the mineralogical composition between the historic and the reconstructed samples may confirm that the proposed methodology may be suitable to be used as a helpful tool in decreasing the analyses error ratios while reconstructing of the archaeological stuccos. This advantage helps in preparing stucco mortars which will be used for the completion of stucco motives, stucco layers pointing, filling of cracks and the standard stucco samples preparation.

The similarity was slightly reduced due to the calcite ratio in the historic sample no.1 in comparison to the other two samples. That may be due to the poor mixing.

Table 2 The cooperative methodology between XRPD analysis and calculation of compounds molecular weight to reconstruct stucco mortar of Sayyida Ruqqya mihrab

The compound	The approximate average ratio of the compound in the three samples%	Calculation of the required ratio of the intermediate phase of the binding material (hemihydrate and calcium hydroxide)	The final ratio of the intermediate phase of the binding material	Notes
Gypsum	62.23	62.23×15.7/100 = 9.77 62.23 - 9.77=52.46	52.46 weight units of hemihydrate	Weight loss is due to the loss of 1.½ H_2O
Bassanite	5.666	--------------------------	5.66 weight units of hemihydrate	The ratio is fixed because it is the required phase
Anhydrite	3.06	3.06×6.62/100 = 0.20 3.06 + 0.20=3.26	3.26 weight units of hemihydrate	The weight increase is due to the addition of ½ H_2O
Calcite	18.466	18.46×26/100=4.799 18.46- 4.799=13.666	13.66 weight units of calcium hydroxide	The weight loss is due to the conversion of calcite to calcium hydroxide
Portlandite	4.566	--------------------------------	4.56 weight units of calcium hydroxide	The ratio is fixed because it is the required phase
Quartz	6.03	------------------------------	6.03 weight units	The ratio is fixed because it will be used as in its original form.
The sum	100%	------------------------------	85.64 weight units	There is a loss of about 14.352 weight units.

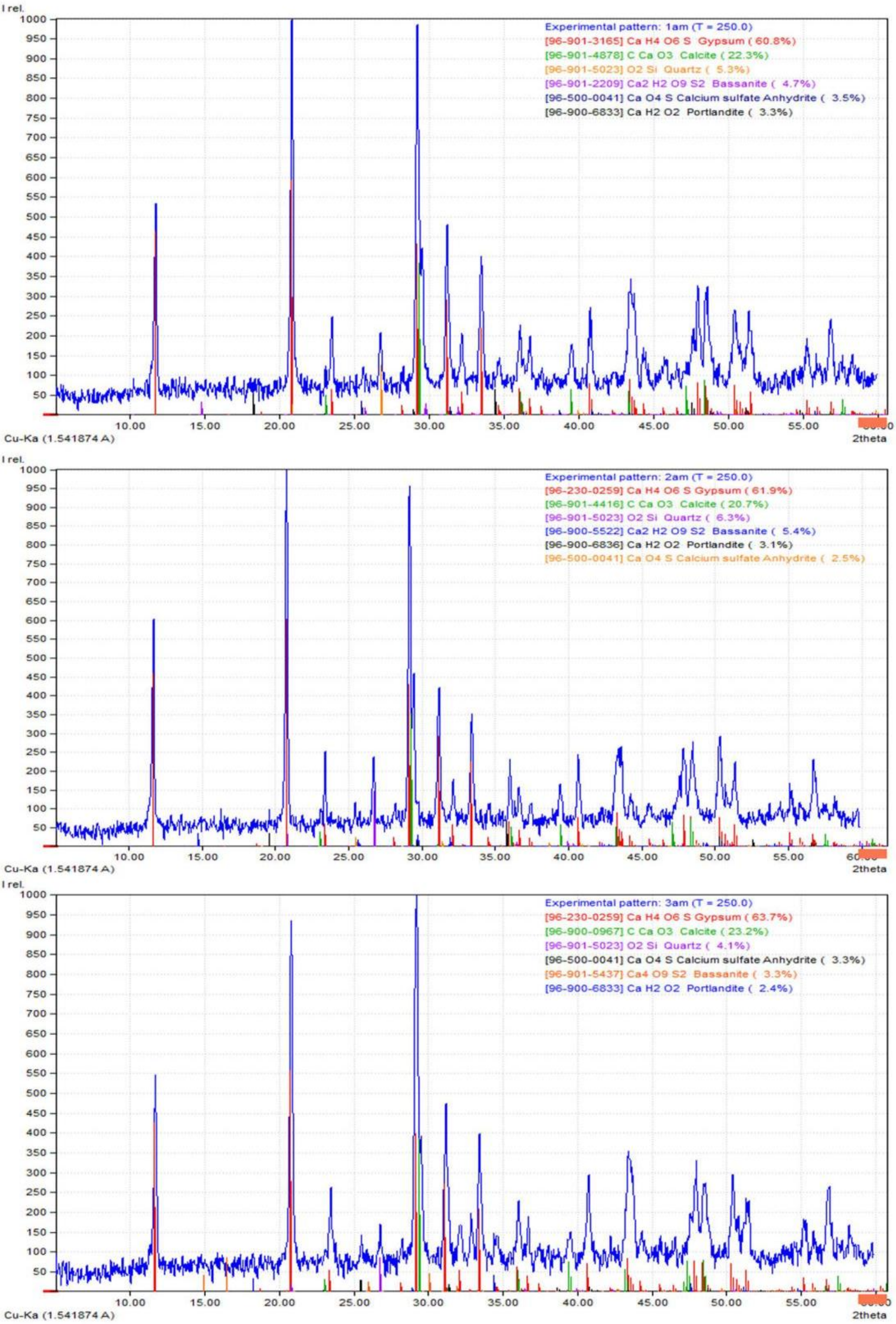

Figure 3 (1am, 2am and 3am) X-ray diffraction patterns of the new reconstructed three stucco samples.

Table 3 The XRPD results of the analyzed three stucco samples of Sayyida Ruqqya main mihrab (historic samples) and the XRPD results of the reconstructed three stucco samples after three months of their casting.

The Compound	XRPD results %	%	%	%	Average ratio % of the compounds
Gypsum	Historic samples	71.2	56.1	59.4	62.23
	Reconstructed samples	60.8	61.8	63.7	62.10
Anhydrite	Historic samples	6.3	7.5	3.2	5.66
	Reconstructed samples	3.5	2.5	3.3	3.10
Bassanite	Historic samples	2.7	4	2.5	3.06
	Reconstructed samples	4.7	5.4	3.3	4.46
Calcite	Historic samples	5.9	22.6	26.9	18.46
	Reconstructed samples	22.3	20.7	23.2	22.06
Portlandite	Historic samples	8.6	1.6	3.5	4.56
	Reconstructed samples	3.3	3.1	2.4	2.93
Quartz	Historic samples	5.4	8.2	4.5	6.03
	Reconstructed samples	5.3	6.3	4.1	5.23

4. Conclusion

The present study illustrated a proposed methodology for the reconstruction of the stucco mortars. This proposed methodology is built on a cooperative relationship between the XRPD analysis and the calculation of the molecular weight of the intermediate and the final phases of binding materials of the historic stucco mortars. The similarity of the XRPD results of the mineralogical composition between the historic stucco samples and the new reconstructed ones may confirm that the proposed methodology may be used as a helpful tool in decreasing the error ratio during the reconstruction of the archaeological stuccos.

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