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DEHYDRATION OF GYPSUM COMPONENT OF PLASTERS AND STUCCOS IN SOME EGYPTIAN ARCHAEOLOGICAL BUILDINGS AND EVALUATION OF K_2SO_4 ACTIVATOR AS A CONSOLIDANT

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ABSTRACT

Studying the aspect of gypsum dehydration is an essential issue. As it has many deteriorating effects on the plasters and stuccos containing gypsum in many Egyptian historic buildings. Especially, in those sites that had been exposed to high temperatures or firing. Thus, this research will try to participate in studying this phenomenon and proposing a method for overcoming it. That was done through a physiochemical study by X ray powder diffraction (XRPD) analysis and scanning electron microscopy-energy dispersive X ray (SEM-EDX) to monitor the conversion of gypsum to anhydrite in historic plaster and stucco samples. Also, it was used to monitor the effect of K_2SO_4 activator solution as a proposed method for reconversion of anhydrite and bassanite to gypsum. The physiochemical study indicated the wide spreading of this aspect. The effect of the anhydrite activator of K_2SO_4 is variable. Sometimes, it increases the conversion of anhydrite to gypsum (Al Alayaa and the Egyptian national theatre samples), in other times did not increase (Habu sample). Moreover K_2SO_4 activator may be a source of a deteriorating salt.

KEYWORDS: Dehydration, stucco, plaster, gypsum, anhydrite, K_2SO_4 activator, conservation

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1. INTRODUCTION

Stucco has been widely used throughout the centuries as decorative coatings for ceiling and walls for both interior and exterior finishing (Falchi et al., 2013). Historic Stucco and plasters are a legacy of our ancestors; they are a very important part of our Egyptian historical building heritage and this reflects the importance of studying and preserving them (Kamel et al., 2015 a).

Architectural Stuccos and plasters in Egypt suffer from the impact of many deterioration factors such as; ground water, salt weathering, defects in support, exposure to high temperature, man-made deteriorations, etc, which have caused complete loss of the decorations of some stuccos and have left others in need of restoration and conservation, so finding solutions for overcoming these deterioration factors and their aspects become ever more urgent.

The stuccos and plasters in general have a tendency to deterioration because of the following properties: **a)** The solubility of the gypsum component (Chapman and Smith-McNally, 1997), **b)** The high porosity of most of stuccos and plasters (Hoffmann and Niesel,1996; Alvarez, 1986; Chapman and Smith-McNally, 1997; Mora et al., 1985); **c)** Differential properties of components; as they may contain many variable components such as; armatures made of metal or wood for support. Moreover, they may contain animal hair, burlap, or plant materials such as; excelsior, hemp, and jute for reinforcement. Sometimes they were protected by surface materials such as; shellac, oil, wax and paint (Chapman and Smith-McNally, 1997). Finally the addition of inorganic materials like brick powder, sand and limestone pieces (Kamel et al. 2015 b). Sometimes, in the severe cases; sand may be the only indicator of plaster and stucco deterioration (Frank, 1971).

One of the widespread deterioration aspects of architectural stuccoes and plasters containing gypsum- as a main binding material- is the conversion of the gypsum content to anhydrite (Kamel et al.2015 b; Kamel et al.2015 a).

Lazarini and Schwartzbaum (1985) had noticed during their study of the Dome of El-Aqsa Mosque in Jerusalem that the gypsum appeared to have undergone a physico-chemical change due to the elevated temperatures of the fire, thus causing the disaggregation of the dome stucco and it was in the process of rapidly falling to pieces.

In Egypt, many studies had detected this aspect in historic plasters and stuccos at many Egyptian periods such as: Aly, (1993); Brania, (2001), Marie, (2004), El-Gohary, (2010), Kamel and Abo El-Yamin, (2018), whom had detected the conversion of the gypsum content to anhydrite in many plasters at many old Egyptian tombs in Aswan, Luxor and Siwa oasis (the approximate ratio of their results is between 24% and 97%).

Kamel had analysed many stucco samples by X-ray diffraction analysis from the minaret of Al Alayaa mosque (11th century A.H /17th century A.D) and the Egyptian national theater (1921 A.D) which was exposed to fire (2008 A.D). He noticed the disappearance of gypsum phase and the clear appearance of anhydrite and bassanite phases.

Kamel et al. (2015b) had detected this aspect in Islamic stucco samples of the Minaret of Shams El-Deen El-Wasty in Cairo; the anhydrite ratio is about 20% wt.

2. CAUSES AND MECHANISM OF GYPSUM CONVERSION TO ANHYDRITE IN HISTORIC STUCCOS AND PLASTERS

Gypsum surfaces are sensitive to excessive dryness as their gypsum component can, at a temperature above 30°C and a moderate R.H. (30–40%); gradually lose its combined water and converts to anhydrite, thus weakening these surfaces (Mora et al., 1985).

Charola and Centeno (2002) considered using 60°C inappropriate in the special case of historic gypsum mortars; as historic gypsum can decompose at temperatures above 40°C. Under normal laboratory conditions, gypsum dehydrates partially, i.e., converting to the metastable hemihydrate $CaSO_4.½H_2O$ at 60°C, and dehydrates most probably into the thermodynamically stable phase anhydrite $CaSO_4$ when heated to 105°C. The conversion of gypsum to anhydrite may be done directly or through intermediate steps forming bassanite and γanhydrite (Kamel et al., 2014).

Gypsum ($CaSO_4.2H_2O$) contains about 20.9% by mass chemically combined water, which is readily lost at an elevated temperature, this phenomenon is called dehydration, the dehydration reaction is endothermic, that is, an amount of energy is needed to break the crystal water (Yuand and Brouwers,2012; Ang and Wang,2009).

Three different mechanisms by which gypsum could be dehydrated to anhydrite:
(a) A solution-precipitation process.
(b) Direct dehydration to anhydrite (loss of structural water).
(c) Stepwise dehydration through the intermediate hydrate, bassanite (Lawrence, 1967).

The transformation of gypsum to anhydrite through intermediate steps forming bassanite and γanhydrite was studied by many researchers such as (Mori, 1986; Klimchouk, 2000; Carbone et al., 2008; Ballirano and Melis, 2009; Milsch et al., 2011).

Although the main cause of the conversion of gypsum to anhydrite is the exposure to high temperature and relative humidity for a long time, there are other reasons that are likely to play a role in the conversion of gypsum in historic stuccos and plasters as; anhydrite 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, β–Anhydrite may have resulted from the overheating of gypsum raw materials during calcination, or as an intentional additive to accelerate setting ,or it may be a result of some or all of the previous possibilities (Kamel et al., 2015 b).

Many sulphate activators such as; K_2SO_4, $Al_2(SO_4)_3$, $FeSO_4$, $CuSO_4$, Na_2SO_4, $ZnSO_4$, $MnSO_4$, $(NH_4)_2SO_4$, Na_2CO_3, $Na_2SO_4 \cdot 10H_20$ and $FeSO_4 \cdot 7H_20$ were studied as activators for natural anhydrite to be a useful building material by activating the dissolution of anhydrite and its conversion to gypsum (Kamel, 1990; Fikry et al., 1996; Kamel, 1996; Singh and Garg, 2000; Sivert et al., 2005; Singh, 2005; Singh and Middendorf, 2007).

In the field of stucco consolidation Kamel et al. (2015a) studied the using of some sulphate activators (K_2SO_4, Na_2SO_4, and $ZnSO_4 \cdot 7H_2O$, 3%w/w in water) in solution form for consolidation of converted gypsum samples to anhydrite by artificial aging. The study results proved that K_2SO_4 activator gave the best results, followed by the Na_2SO_4 activator. Although the $ZnSO_4 \cdot 7H_2O$ activator succeeded in transforming anhydrite but without giving satisfactory mechanical results; this may be related to the shapes of the non-interlocked gypsum crystals.

This paper will evaluate the effect of K_2SO_4 activator on real converted archaeological stucco and plasters samples to anhydrite by using of some examination and analysis methods.

3. MATERIALS AND METHODS

3.1 Sampling

Three samples were collected carefully, using a micro-scalpel, to identify the constituents and degree of conversion of the gypsum content of the deteriorated stucco and plasters of the Habu temple, the minaret of Al Alayaa mosque and the Egyptian national theatre. All the analysed and investigated samples were carefully collected from severely damaged and fallen parts (Table 1).

Table 1: Description of the analysed and investigated samples collected from the three studied sites.

Sample code.	Sample description(all samples locations were shown in fig.(1)
abdBha	Deteriorated plaster sample taken from the Habu temple before application of K_2SO_4 solution.
abdAha	The same sample of the Habu temple but after application of K_2SO_4 solution.
abdBal	Fragile stucco sample taken from the minaret of Al Alayaa mosque before application of K_2SO_4 solution.
abdAal	The same sample of the minaret of Al Alayaa mosque but after application of K_2SO_4 solution.
abdBth	Fragile stucco sample taken from the Egyptian national theater before application of K_2SO_4 solution. This site had been subjected to fire.
abdAth	The same sample of the Egyptian national theater but after application of K_2SO_4 solution.

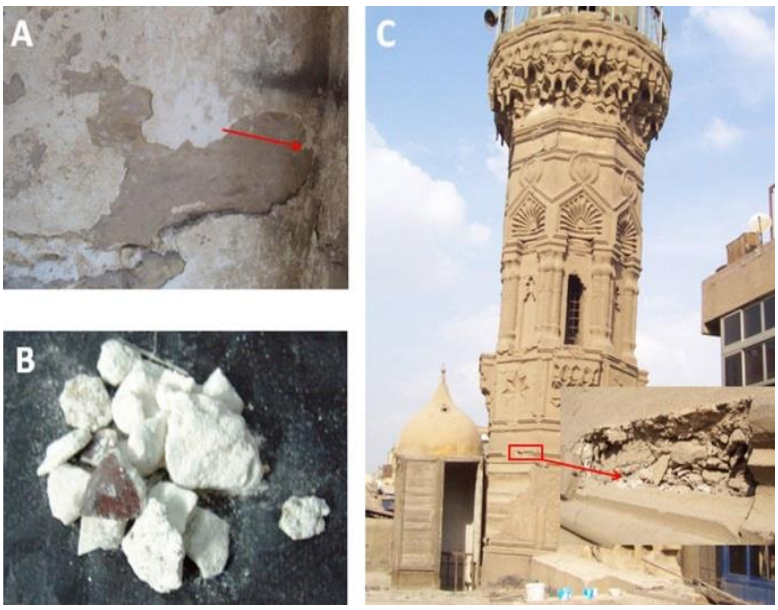

Figure 1. shows the studied plaster and stucco samples (A) the approximate location of the fragile small sample of the Habu temple, (B) the fallen stucco samples of the Egyptian national theater after subjection to fire, (c) the approximate location of the fragile small stucco sample of the minaret of Al Alayaa mosque.

3.2 X-ray powder diffraction (XRPD)

The X-ray diffraction patterns of the stucco and plaster powders of the three samples were obtained using a diffractometer type (XPERT – PRO – PANalytical – Netherland). The reference data base used for matching is PDF-4+2015RDB. The analyses were done before and after application of potassium sulphate solution.

3.3 Scanning electron microscopy (SEM)

The morphology and microstructure of the mineral constituents in the three stucco samples were recorded - before and after application of potassium sulphate - with a scanning electron microscope: Model Quanta FEG 250 attached with EDX unit (Energy Dispersive X-ray Analyses), with accelerating voltage 20 k.V., without coating the samples with a highly conductive thin film of gold. The SEM.EDX was done at the national research center, Giza, Egypt.

3.4 The application of (K_2SO_4) activator on the archaeological stucco and plaster samples.

The selected sulphate activator solution - (K_2SO_4) 3%w/w in water- was applied by brushing on the surfaces of stucco and plaster samples, until surface saturation for one time. All steps were monitored by XRD and SEM-EDX.

4. RESULTS AND DISCUSSION

4.1 X-ray powder diffraction (XRPD)

The XRPD patterns of the analysed stucco and plaster samples of the studied sites are resumed in Table 2.

Table 2. The approximate XRD analysis results of stucco and plaster samples of the studied sites before and after application of potassium sulphate.

The Component%	Habu before K_2SO_4	Habu after K_2SO_4	Al Alayaa before K_2SO_4	Al Alayaa after K_2SO_4	National theater before K_2SO_4	National theater after K_2SO_4
Gypsum	4.2	4	4.6	27.6	33.4	95.7
Bassanite	-		-	-	46.3	-
Anhydrite	63.2	53.7	83.9	56	3.3	3.3
Calcite	27.2	35.7	5.6	5.1	-	-
Portlandite	5.3	2.1	-	-	-	-
Quartz	-	4.9	5.9	11.3	9.7	0.9

The results resumed in Table 2 indicate the following results of the semi-quantitative analysis of the mineralogical components of stucco and plaster samples:

- In the Habu plaster sample, the application of potassium sulphate solution has not any remarkable conversion from anhydrite to gypsum. As the decrease of anhydrite ratio relates to the increase of calcite and quartz ratios not to the phase conversion of anhydrite to gypsum, (Fig.2).
- In Al Alayaa stucco sample, an increase of anhydrite conversion to gypsum was detected. As the increase of gypsum ratio is about 23% and the decrease of anhydrite ratio is about 28%, (Fig.3).
- In the stucco sample of the Egyptian national theater, the disappearance of bassanite as well as the remarkable increase of gypsum may confirm the effect of potassium sulphate solution as a method for reconversion of bassanite and anhydrite to gypsum phase (Fig.4).

We can conclude from the previous three results that there is an inverse correlation between the conversion rate of anhydrite to gypsum and the ratio of calcite phases. That may be confirmed by what mentioned by Kamel (1990) and Marie (2004) that there are many factors, which control the gypsification process (anhydrite solubility and its conversion to gypsum) such as; solution pH value and salinity. These factors may have a negative effect on the solubility of anhydrite. In the Habu plaster sample, the CO_3^- anion and other anions may make the conversion reaction of anhydrite a reverse reaction.

4.2 Scanning electron microscopy (SEM)

- The observations made by using SEM for the untreated and the treated sample of the Habu plaster with K_2SO_4 showed that no noticeable change in the crystallographic forms of gypsum. That may confirm the results of XRPD. But while scanning the treated sample surface many efflorescence spots of elongated crystals were detected. The appearance of (K), (S) and (O) elements in EDX analysis may confirm that it is potassium sulphate salt, (Figs.5 and 6). This salt was not detected by XRPD, which may be related to its very low percentage in the ground sample. The appearance of this efflorescence may indicate the low porosity of surface of plaster sample. This point of discussion may confirm that potassium sulphate activator sometimes may be a source of deterioration as a salt.
- The observations made by using SEM for the untreated and the treated sample of Al Alaaya stucco with K_2SO_4 showed the appearance of the interlocked needle-like crystals, which may be related to the reformation of gypsum crystals by the catalysing of K_2SO_4 solution, (Fig.7). That result was confirmed by XRPD analyses results.
- The obvious appearance of the interlocked needle-like crystals in the treated stucco sample of the Egyptian national theater confirms the conversion of the intermediate phase to gypsum (Fig.8).

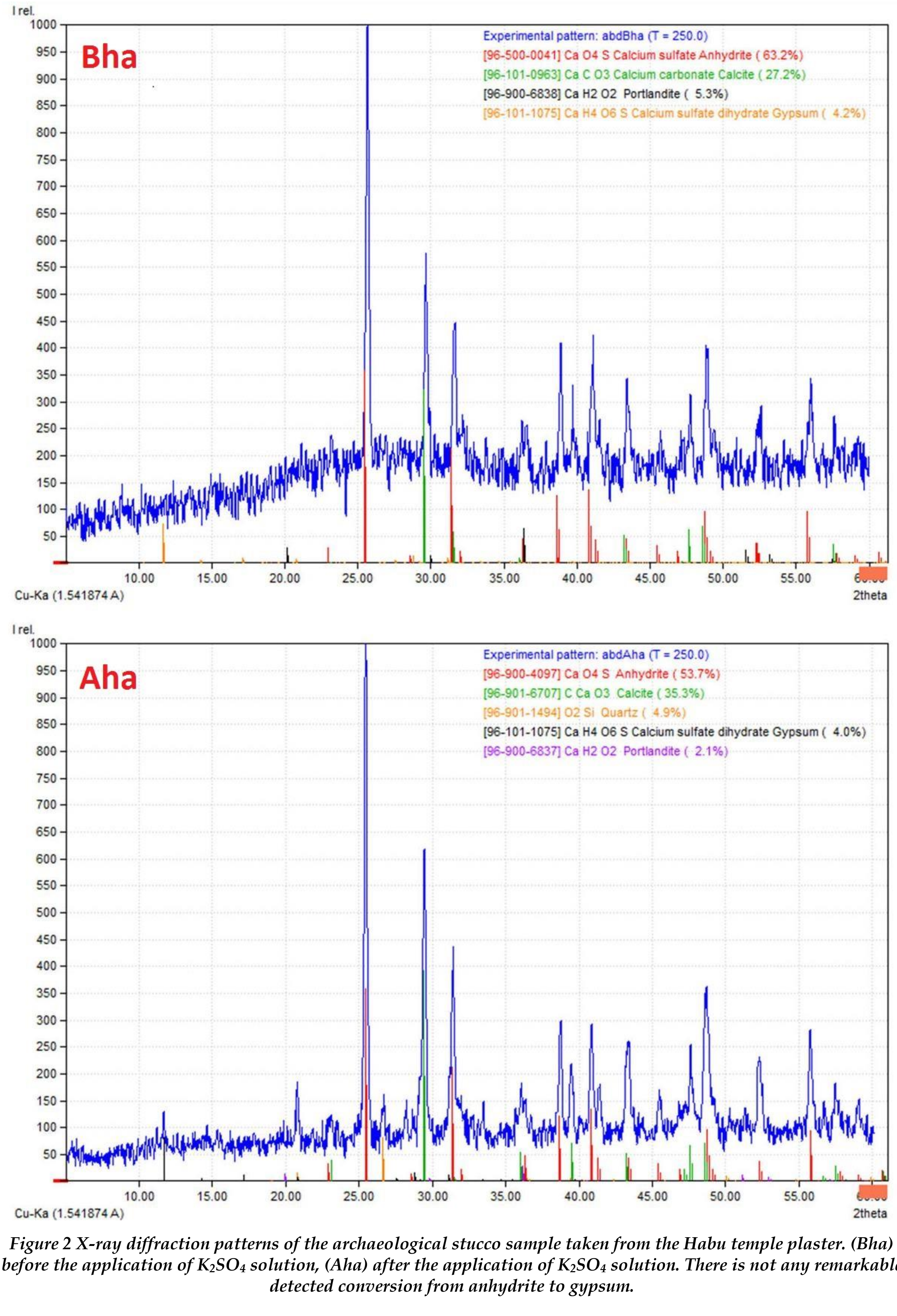

Figure 2 X-ray diffraction patterns of the archaeological stucco sample taken from the Habu temple plaster. (Bha) before the application of K_2SO_4 solution, (Aha) after the application of K_2SO_4 solution. There is not any remarkable detected conversion from anhydrite to gypsum.

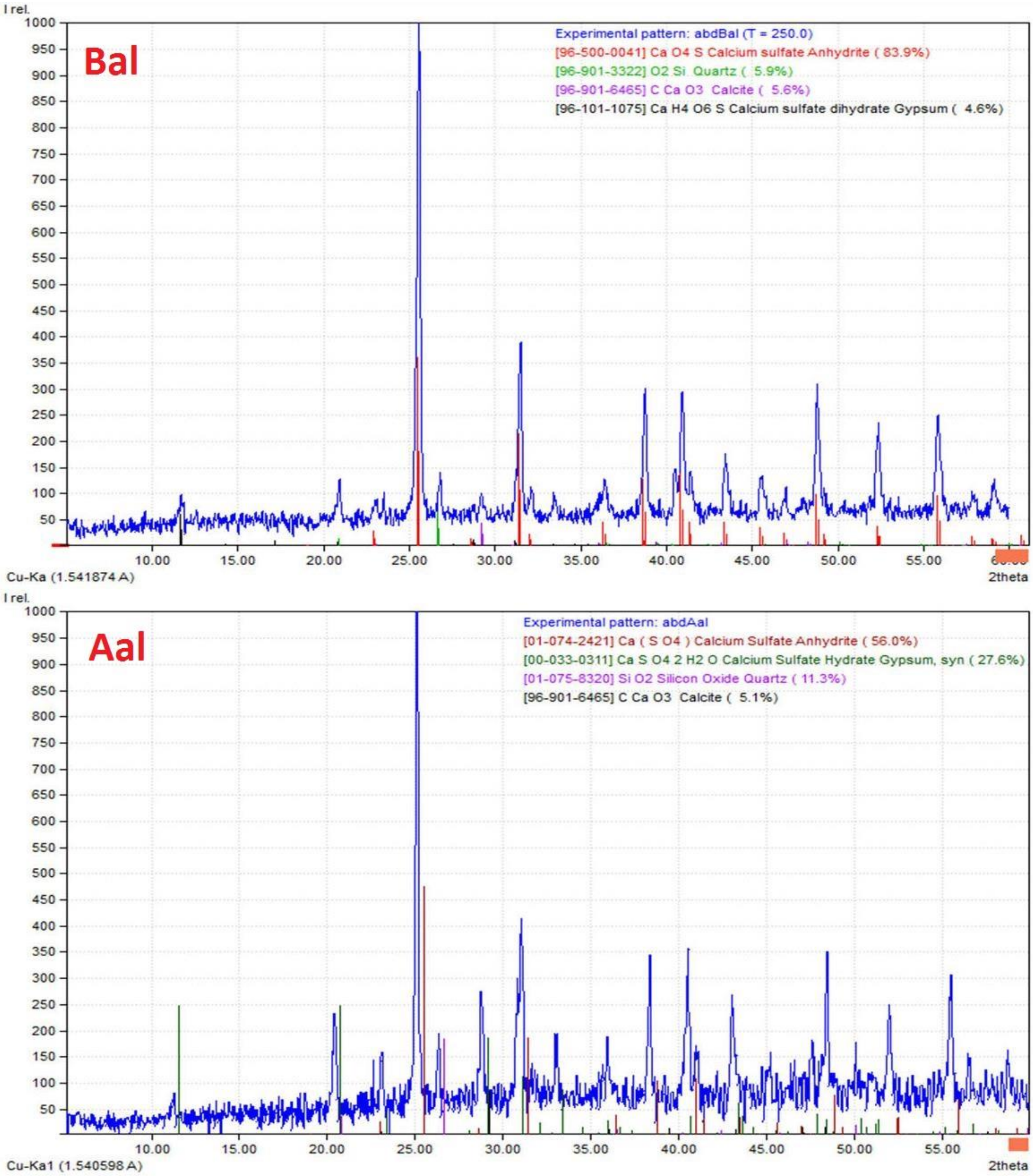

Figure 3 X-ray diffraction patterns of the archaeological stucco sample taken from the Al Alayaa minaret. (Bal) before the application of K_2SO_4 solution, (Aal) after the application of K_2SO_4 solution. The results show the effect of potassium sulphate solution for increasing of anhydrite conversion to gypsum.

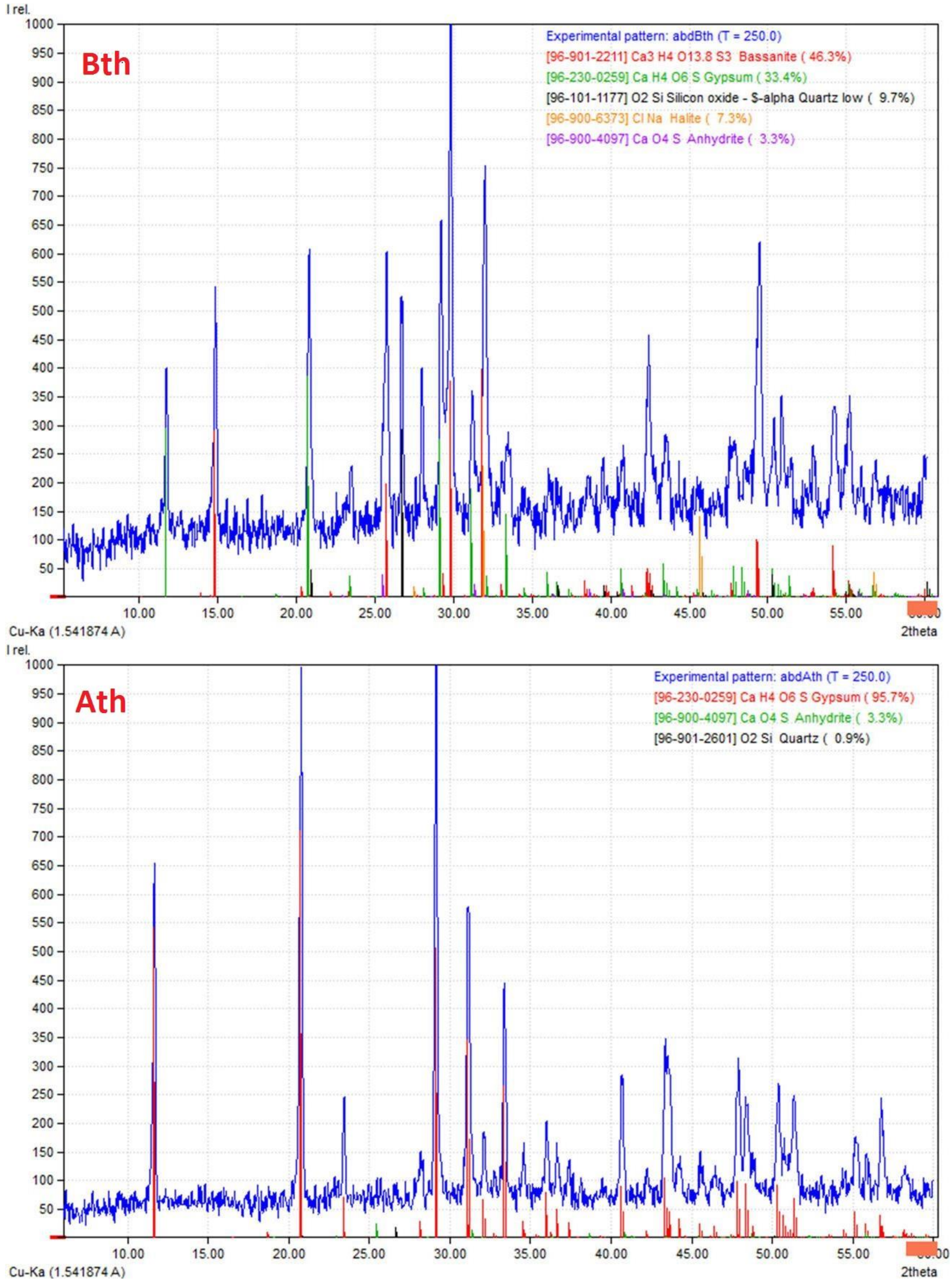

Figure 4 X-ray diffraction patterns of the archaeological stucco sample taken from the Egyptian national theater. (Bth) before the application of K_2SO_4 solution, (Ath) after the application of K_2SO_4 solution. The results show the disappearance of bassanite as well as the remarkable increase of gypsum.

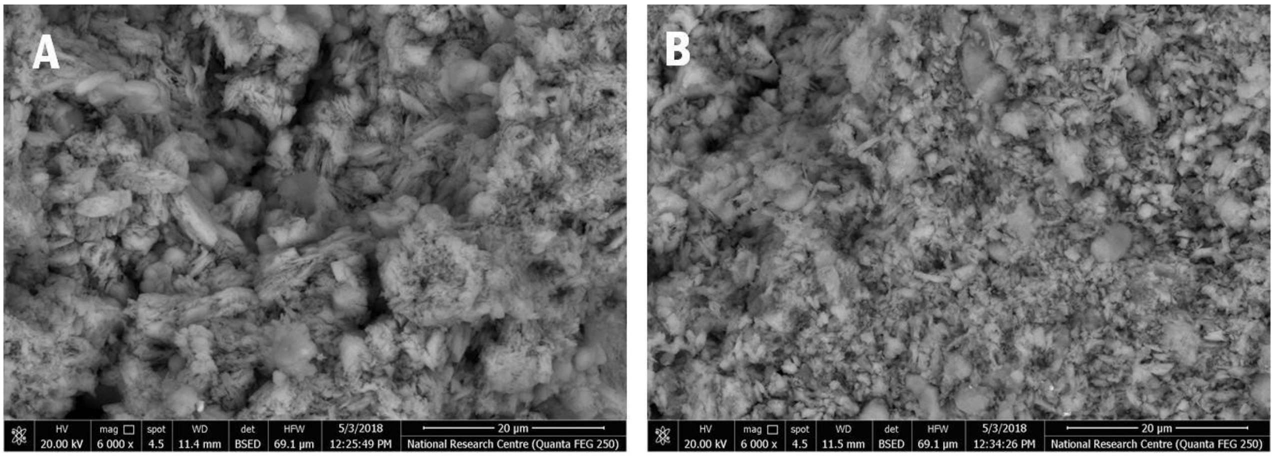

Figure 5 Scanning electron micrographs of the untreated sample (A) and the treated sample (B) of the Habu plaster with K_2SO_4 solution show that no noticeable change in the crystallographic forms.

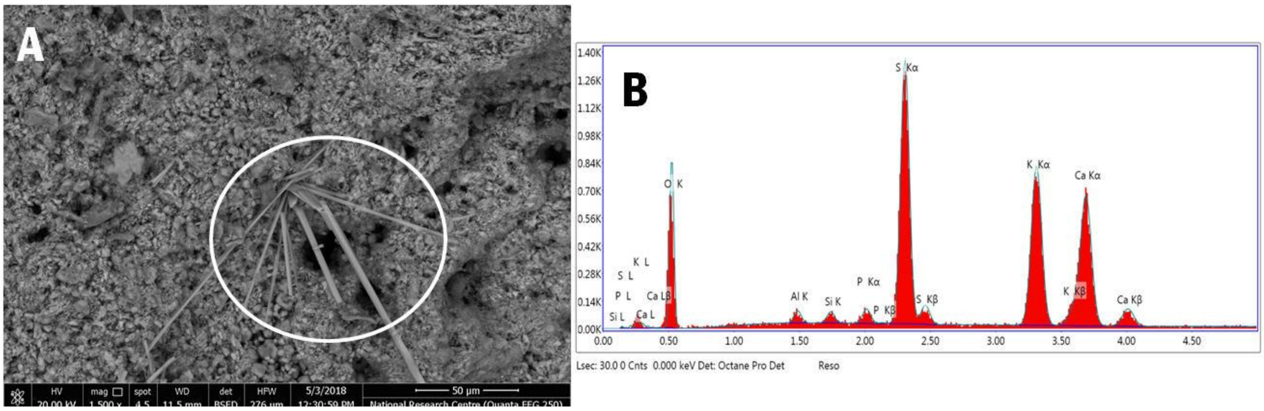

Figure 6 (A) Scanning electron micrograph of the efflorescence spots of the elongated crystals which were detected on the Habu sample surface. (B) EDX spectra results of the elongated crystals show the appearance of (K), (S) and (O) elements which may confirm that it is potassium sulphate salt.

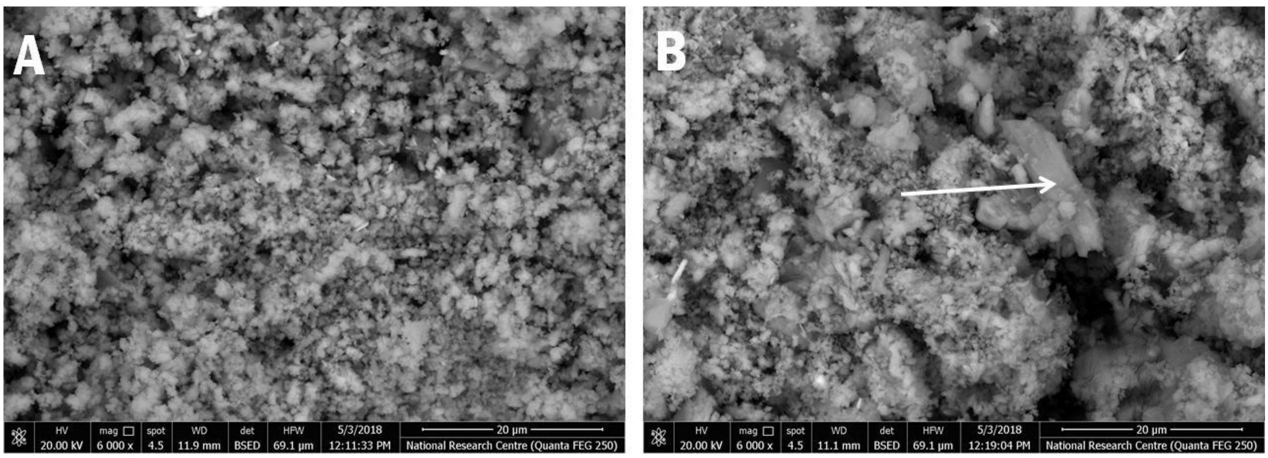

Figure 7 Scanning electron micrographs of the untreated sample (A) and the treated sample (B) of the Al Alaaya stucco with K_2SO_4 solution showed the appearance of the interlocked needle-like crystals, this may be related to the reformation of gypsum crystals.

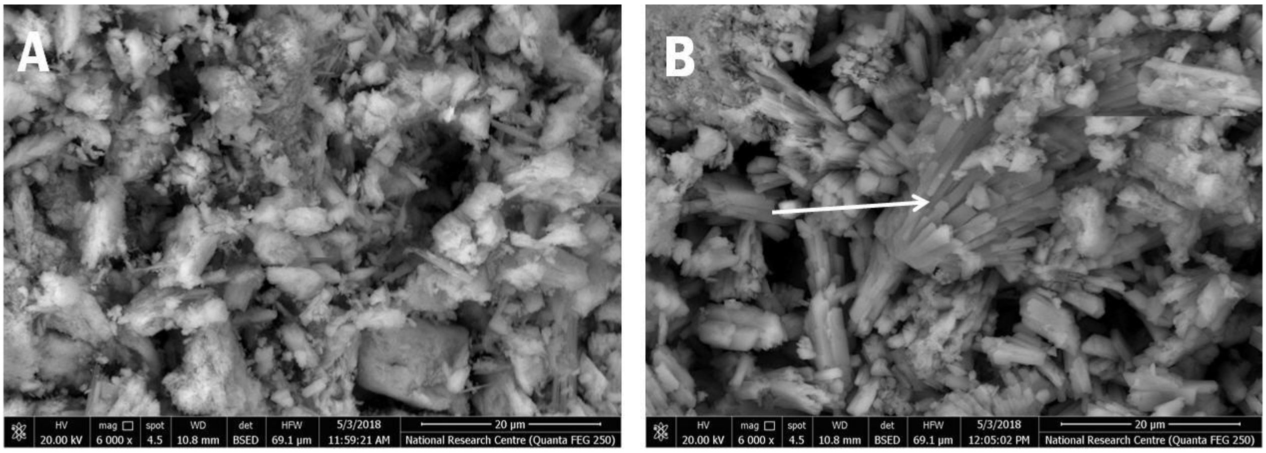

Figure 8 Scanning electron micrographs of the untreated sample (A) and the treated sample (B) of the Egyptian national theater with K_2SO_4 solution show the obvious appearance of the interlocked needle-like crystals which confirms the conversion of the intermediate phase to gypsum crystals.

5. CONCLUSION

The aspect of gypsum conversion to anhydrite in historic stucco and plasters is very important, as it plays an effective role in their deterioration. The XRPD analysis of many samples from many Egyptian historic sites confirmed the wide spreading of this aspect. The XRPD analysis and SEM.EDX of the treated historic samples - the deteriorated stucco and plasters of the Habu temple, the minaret of the Al Alayaa mosque and the Egyptian national theater - by K_2SO_4 solution confirmed that anhydrite activator of K_2SO_4 solution sometimes causes the increase of anhydrite conversion to gypsum. Especially as noticed with gypsum historic samples of the Al Alayaa and the Egyptian national theater samples. Other times, the presence of other anions or lower surface porosity may reduce the conversion effect. The K_2SO_4 activator solution may be a source of deterioration by salts as many K_2SO_4 salt efflorescence spots were noticed on the surface of Habu treated sample.

The conclusions confirm that the use of K_2SO_4 activator as a method for anhydrite conversion to gypsum until now has given indeed hesitating results. As there are many factors could affect the results such as; solution pH value and salinity.

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