EVALUATION OF SULPHATE ACTIVATORS AS CONSOLIDANTS FOR THE TRANSFORMED GYPSUM IN HISTORIC STUCCO

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Abstract

Stucco monuments suffer from many causes of deterioration; one of these is the transformation of the gypsum content of stucco to anhydrite, which causes disintegration and the appearance of fine fissures that sometimes culminate in the complete loss of archaeological stucco material; this problem makes thinking of a new protocol for its treatment very urgent. So the research proposes using sulphate activators, which may lead to retransformation of anhydrite to gypsum and thus will participate in protecting our stucco heritage. Many parameters have been used; including XRPD analysis, XRF, FTIR, measurement of physical and mechanical properties, SEM and aging by sodium chloride. All results proved that sulphate activator solutions have the ability to retransform anhydrite to gypsum and to increase the mechanical strength of stucco material.

Keywords: *Anhydrite; Consolidant; Gypsum; Stucco; Sulphate activators.*

Introduction

Stucco monuments 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. One of the urgent problems in preserving stucco monuments is the transformation of the gypsum content of stucco to anhydrite.

Gypsum surfaces are sensitive to excessive dryness. In effect, the gypsum can, at a temperature above 30ºC and a moderate R.H. (30–40%), gradually lose its combined water and become anhydrite, thus weakening the rendering [1]. This phenomenon was proved during the study of the Dome of El-Aqsa Mosque in Jerusalem, where it was noticed that the gypsum appeared to have undergone a physico-chemical change due to the elevated temperatures of the fire, thus leaving the stucco, at best, in a poor condition and with poor adhesion and, at worst, completely disaggregated and in the process of rapidly falling to pieces [2].

E.L. Charola and S.A. Centeno [3] considered using 60ºC inappropriate for the special case of historic gypsum mortars, as historic gypsum can decompose at temperatures above 40ºC. Under normal laboratory conditions, gypsum dehydrates partially, i.e., converting to the metastable hemihydrate $CaSO_4.\frac{1}{2}H_2O$ at 60ºC, and dehydrates most probably into the thermodynamically stable phase anhydrite $CaSO_4$ when heated to 105ºC.

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In Egypt, numerous studies have proved the transformation of archaeological gypsum to anhydrite (the approximate ratio of their results is between 13% and 97%) [4-10].

Many studies had been done on the activation of anhydrite by sulphate activators; as three chemical activators were used by *A.M.A. Kamel* in 1990 [11] to activate the transformation of natural anhydrite (Ras Malaab Area) into gypsum. These chemical activators are $(NH_4)_2SO_4$, Na_2SO_4, and Na_2CO_3, the first two activators led to the absence of anhydrite crystals, which causes high strength and low values of water absorption. Also, the microscopic results came to prove the data of the XRD analysis and DTA. It was found that the use of Na_2CO_3 led to reversing the reaction (Gypsum anhydrite) [11].

Gypsum anhydrite-slag mixtures that were produced by blending anhydrite with granulated blast furnace slag, $Ca(OH)_2$, and small amounts of $Na_2SO_4 \cdot 10H_2O$ and $FeSO_4 \cdot 7H_2O$ as activators were studied by *M. Singh and M. Garg* [12] who noticed that the plausible mechanism for the attainment of high strength in the anhydrite-slag mixture is due to rapid conversion of anhydrite into gypsum, through formation of double salts with the activators and due to formation of ettringite and tobermorite compounds.

The chemical activators: K_2SO_4, $Al_2(SO_4)_3$, $FeSO_4$, $CuSO_4$, Na_2SO_4, $ZnSO_4$, $MnSO_4$, and $(NH_4)_2SO_4$ were used as accelerator salts to convert anhydrite to a useful building material by partially transforming it to gypsum at concentrations of 1, 2 and 3% by weight [13]. *A.M.A. Kamel* [14] also discussed the effects of K_2SO_4, $ZnSO_4$, and $MnSO_4$, as accelerators on Egyptian anhydrite by partial conversion of anhydrite to gypsum, and noted that these activators have the ability to transform anhydrite into gypsum.

The results of studying the effects of different chemicals on setting and hardening of anhydrite cement and its hydration characteristics showed that the use of sodium sulfate and ferrous sulfate activators achieved the maximum attainment of strength, also, microscopic studies revealed that formation of euhedral, prismatic and rhombic gypsum crystals govern the high strength development in anhydrite cement [15].

The hydration of anhydrite ($CaSO_4$) in a ball mill as a function of time and temperature was studied by *T. Sivert et al.* [16], who concluded that in the presence of activators, the time for maximum rate of gypsum formation and maximum specific surface area shifted towards a lower hydration time. Also, he made a detailed mechanism of anhydrite hydration. While Singh described the effect of the K_2SO_4 activator on the hydration of chemical anhydrite obtained from burned FGD-gypsum and concluded that the results obtained showed a degree of hydration increase when the K_2SO_4 concentrations increase from 0.5 to 3.3wt%. The X-ray and SEM/EDX studies have shown that K_2SO_4 is adsorbed at the surface of $CaSO_4$ even within five minutes of hydration and a syngenite (a double salt $K_2SO_4 \cdot CaSO_4 \cdot H_2O$) is formed (even in the presence of 1.0wt% K_2SO_4). Also, important changes in the morphology of the dihydrate crystal are detected [17]. In another paper of *N.B. Singh and B. Middendorf* [18] studied the accelerating effect of various anions and cations on hemihydrate hydration and they found that K_2SO_4 is the most effective accelerator. It is believed that K_2SO_4 accelerates the hydration by increasing the rate of hemihydrate dissolution.

This paper suggests the possibility of using sulphate activators in solution form for consolidation of gypsum monument surfaces (that suffer from partial or complete transformation of gypsum to anhydrite),that was built on the success of using them to transform natural anhydrite into a useful building material by activating the dissolution of anhydrite and it's conversion to gypsum, so the paper will analyze the possibility of using sulphate activator solutions as a consolidant for the transformed gypsum in archeological stucco by retransforming anhydrite to gypsum.

Materials and methods

Preparation of the experimental stucco samples

Two kinds of stucco samples ($5cm^3$) were prepared to express the Egyptian stucco; gypsum stucco and gypsum lime stucco. The gypsum material was produced by Gypsina Company, according to Egyptian Standards, no. 188 (2005), while gypsum lime stucco was built on the final results of the XRPD Analysis of three stucco samples were collected from the stucco niche of the dome near the Khankaa of Idekene El Bendekdary (an Islamic monument from the Mamluk period, 1285); the final results of the mineralogical components, which were prepared after converting the final phases gypsum and calcite of binding materials to the intermediate phases hemihydrates and calcium hydroxide were 53 parts of hemihydrate by weight, 27 parts of calcium hydroxide by weight and three parts of sand by weight, were used in the mix of gypsum lime stucco. Gypsum stucco samples were prepared by mixing gypsum powder with water by hand (gypsum powder = hemihydrate): the binder: water ratio was 3:2 by volume ± 5%. Samples were then prepared by molding the paste to 5cm cubics. But gypsum lime stucco samples were prepared by the dry mixing of slaked lime powder $Ca(OH)_2$, gypsum (hemihydrate and sand, the powder mix was then prepared with the same specifications. All stucco samples were kept for ten months in the surrounding atmospheric conditions. The transformation of calcium hydroxide was monitored by XRD and FTIR analysis after ten months.

Transforming the gypsum content of stucco samples to anhydrite

This partial or complete transformation was done by exposing the two kinds of stucco samples to a range of temperatures of about 300ºC ±10, for six hours in an oven, this range was built on the works of more authors [19-21], it was also built on experimental tests carried out by the authors, as they tested gradually using different degrees of heat (200, 250 and 300ºC) and periods (2, 4 and 6 hours). The tests were monitored by XRPD, until a suitable amount of β-anhydrite appeared.

The application of the selected chemical activator solutions

Three selected chemical activators solutions (K_2SO_4, Na_2SO_4, and $ZnSO_4 \cdot 7H_2O$) 3%w/w in water, were applied by spraying on the surfaces of stucco samples, until surface saturation for one time, all steps were monitored by XRD, XRF analysis, and SEM examination.

X-ray Diffraction Analysis (XRPD)

The X-ray diffraction patterns of the stucco powders were obtained using a diffractometer type (PW 1840,Philips,Netherlands), operated at 40 kV, using a Cu Kα radiation wavelength of 1.54053Å. The measurements were made at room temperature. Preparation of each sample consisted of grinding it to obtain a fine powder.

Fourier Transform Infrared Analysis (FTIR)

IR spectra were obtained using a spectrophotometer (FTIR, 4100, JAFCO, JAPAN). The sample preparation process consisted of grinding the sample to obtain fine stucco powder which was then mixed with KBr powder.

X-ray Fluorescence analysis (XRF)

Twenty stucco samples were analyzed by XRF from standard samples, aged samples and treated samples to determine the ratio of the elemental oxides related to the use of sulphate activators solutions.

Scanning Electron Microscopy (SEM)

The microstructure and morphology of mineral constituents in the stucco samples were recorded with a Scanning Electron Microscope (Jeol JSM 5200, Japan). The microscope was operated at 25kV accelerating voltage. Sample preparation consisted of application of a superficial gold film by sputtering to prevent electrostatic charge.

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Measuring of physical and mechanical properties

Physical and mechanical properties such as; bulk density, water absorption, apparent porosity, dry and wet compressive strength, were measured before and after the aging of stucco samples and after application of chemical activators. Bulk density, water absorption and apparent porosity were measured with the aid of ASTM.C20-46 but the dry and wet compressive strength, were measured by Form-test/Prufsysteme/Zwiefalter strape20/D-88499 Riedlingen.

Artificial aging by sodium chloride

Aging cycles were carried out according to (RILEM 25-PEM -1980) [22]. This salt was selected because it is one of the most harmful salts present at archaeological sites in Egypt and is the principal deteriorating salt in research applications.

Results and discussion

X-ray Diffraction Analysis (XRD) and FTIR

The X-ray diffraction patterns of the gypsum lime stucco samples (which were prepared for the experimental study) after 10 months of exposure to room atmospheric conditions indicate that most of the portlandite ratio was converted to calcium carbonate as a result of the surrounding atmosphere, especially carbon dioxide gas (Fig. 1). The XRD results were proved by the results of FTIR analysis, (Fig. 2).The comparison between the bands of $1437cm^{-1}$ with $1426cm^{-1}$ and the band $872cm^{-1}$ with $874cm^{-1}$ allows the identification of $CaCO_3$ and the increase of its ratio after 10 months.

The X-ray diffraction patterns of the gypsum and gypsum lime stucco samples that were exposed to temperature degree $300^{\circ}C \pm 10$ for six hours, in comparison with the non-heated samples show the transformation of gypsum content to anhydrite and other intermediate phases of gypsum (Figs. 3 and 4). After this point of transformation, the samples were ready for the application of sulphate activators solutions.
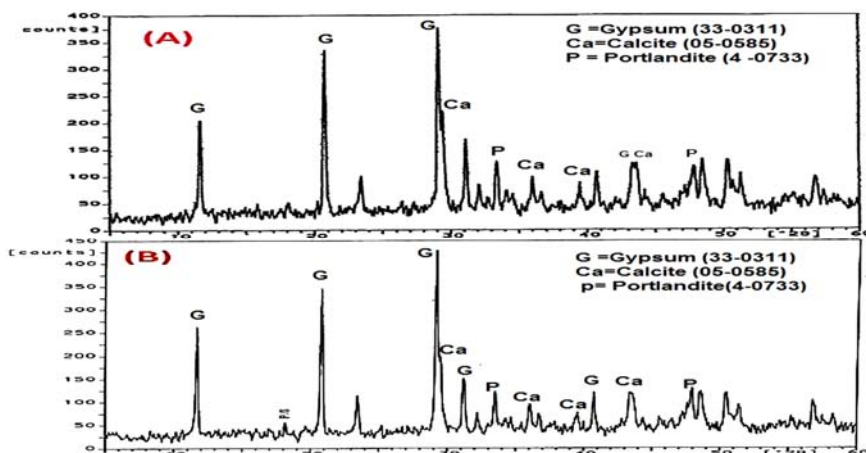

Fig. 1. X-Ray diffraction patterns of the gypsum lime stucco samples after 10 months of room atmospheric conditions exposure, most of portlandite ratio was converted to calcium carbonate.
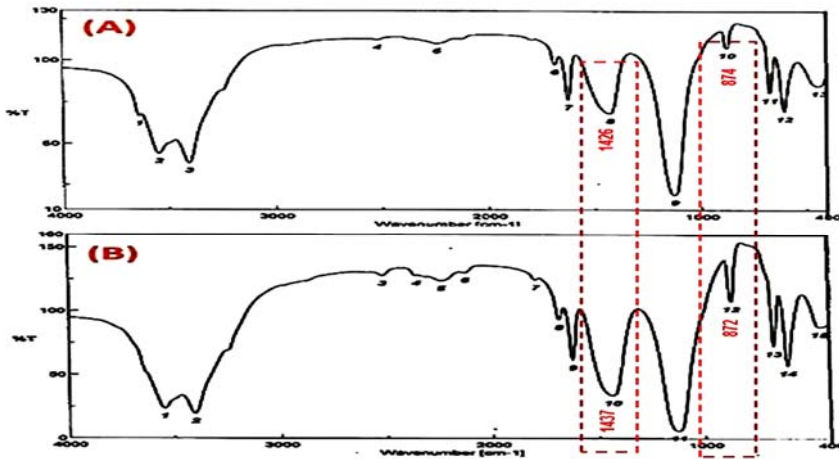
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Fig. 2. FTIR spectra from the gypsum lime stucco samples (A) after 1 month (B) after 10 months, bands related to CO_3 prove the results of XRD analysis.
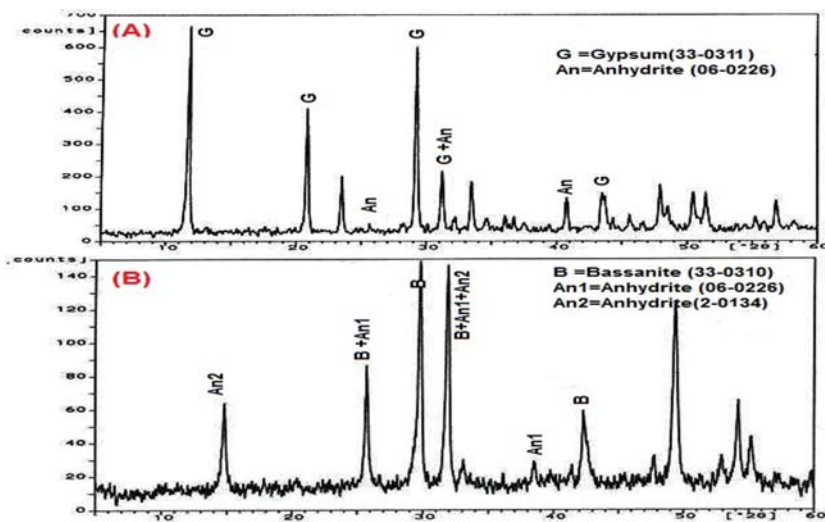

Fig. 3. The X-ray diffraction pattern of the gypsum stucco samples that were exposed to a temperature of $300^{\circ}C \pm 10$ for six hours, in comparison with the non-heated gypsum sample. The figure shows the transformation of gypsum content to anhydrite and other intermediate phases of gypsum.

The X-ray diffraction patterns of the treated gypsum and gypsum lime stucco samples with the selected sulphate activators solutions (after more than 28 days in comparison with the untreated samples) showed the appearance of gypsum and the approximate disappearance of anhydrite (Figs. 5 and 6) that emphasized the ability of the selected sulphate activators solutions to retransform anhydrite to gypsum, which may increase the strength of the stucco samples. Fortunately, none of the three compounds; potassium carbonate, sodium carbonate or zinc carbonate, was detected in the X-ray diffraction patterns of the treated samples, which decreases the possibility of formation of harmful salts, or reaction of sulphate activators with the other components of the stucco, such as calcium carbonate.
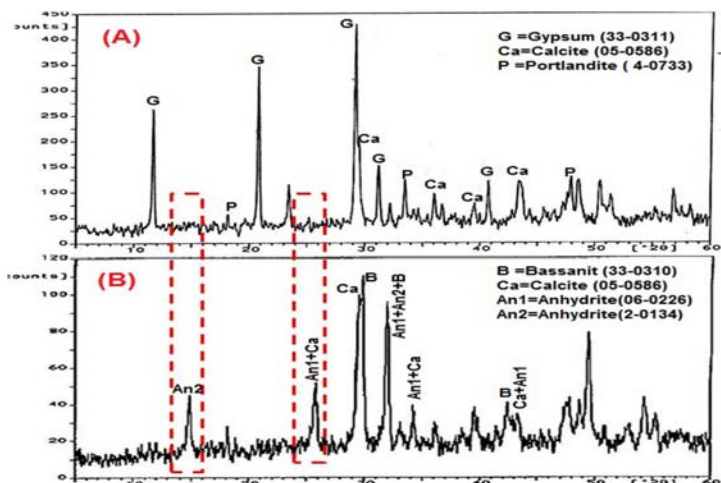
Fig. 4. The X-ray diffraction pattern of the gauged stucco samples which were exposed to a temperature of 300ºC ± 10 for six hours, in comparison with the non-heated gauged sample, the figure shows the transformation of gypsum content to anhydrite and other intermediate phases of gypsum.
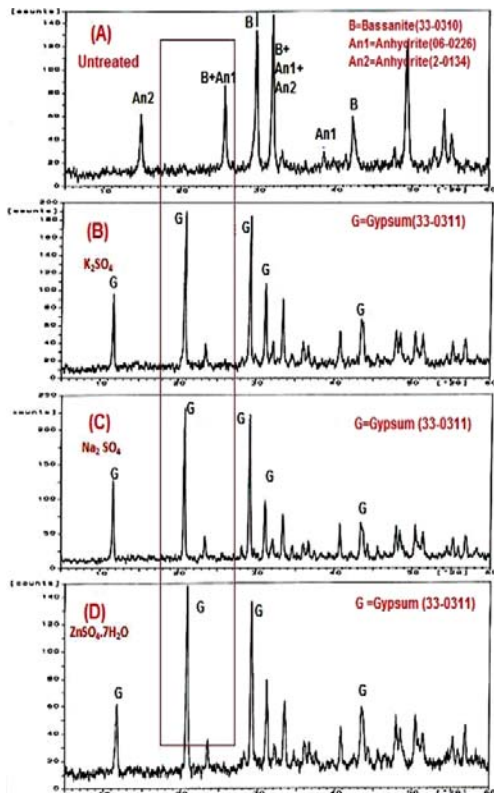

Fig. 5. The X-ray diffraction patterns of the treated gypsum stucco samples with the selected sulphate activators solutions, after more than 28 days, in comparison with the untreated sample, the patterns indicate the appearance of gypsum and the approximate disappearance of anhydrite
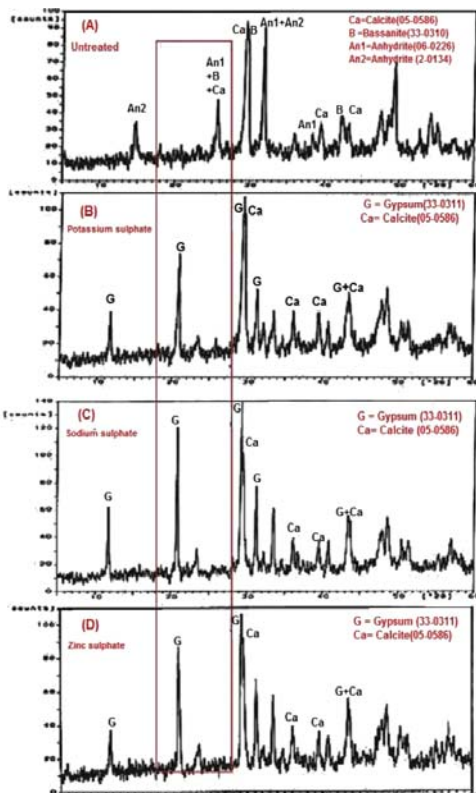
Fig. 6. The X-ray diffraction patterns of the treated gauged stucco samples with the selected sulphate activators solutions, after more than 28 days, in comparison with the untreated sample, the patterns indicate the appearance of gypsum and the approximate disappearance of anhydrite

X-ray Fluorescence Analysis (XRF)

According to the results shown on the following table, all the elemental oxides related to the use of sulphate activator solutions are still in the range of traces (i.e., do not exceed 0.45%) and that decreases the possibility of formation of harmful salts or a reaction with the other components of the stucco such as calcium carbonate (Table 1).

Scanning electron microscopy (SEM)

The observations made by using SEM for the treated gypsum stucco samples showed the appearance of interlocked needle-like crystals, which may be related to the reformation of gypsum crystals in all the treated gypsum stucco samples with the selected sulphate activators (Figs. 7 and 8). This may cause an increase of cohesion among crystals (that will be proved by measurement of the physical and mechanical properties), also, in the micrographs of the treated gauged stucco samples with the selected sulphate activators, the appearance of some elongated crystals may be related to the reformation of gypsum crystals (Figs. 9 and 10). However, in the samples treated with Na_2SO_4, some mineral crystals were found among the elongated gypsum crystals may be related to the formation of sodium chloride crystals as proved by XRD analysis (Fig. 8C and 8D; Fig. 10C and 10D).

Table 1. The XRF analysis results of the standard and treated stucco samples with the selected sulphate activators.

| Sample name/element oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	SrO	Loss	Total
Standard mix before aging and treatment	0.34	0.04	0.11	39.94	0.08	51.65	0.01	0.01	0.01	0.01	0.26	7.48	99.92
Standard mix before aging and treatment	1.36	0.01	0.13	37.57	0.07	53.26	0.01	0.01	0.01	0.01	0.24	7.26	99.93
Standard mix before aging and treatment	1.37	0.05	0.17	44.04	0.21	30.32	0.02	0.02	0.01	0.02	0.21	23.35	99.79
Standard mix before aging and treatment	1.34	0.04	0.14	40.35	0.20	32.05	0.02	0.02	0.01	0.02	0.19	25.53	99.90
Standard gypsum after artificial aging by temperature	0.25	0.03	0.04	38.74	0.06	51.84	0.01	0.01	0.01	0.01	0.24	8.58	99.81
Standard gypsum after artificial aging by temperature	0.77	0.01	0.07	36.69	0.05	55.56	0.01	0.01	0.01	0.00	0.24	6.53	99.94
Standard gypsum after artificial aging by temperature	2.18	0.08	0.15	42.76	0.28	35.25	0.01	0.02	0.01	0.02	0.18	18.87	99.82
Standard gypsum after artificial aging by temperature	1.29	0.03	0.13	44.52	0.16	34.62	0.02	0.03	0.01	0.02	0.21	18.87	99.90
K_2SO_4 gypsum	0.17	0.03	0.05	35.03	0.04	45.07	0.01	0.45	0.01	0.00	0.24	18.89	99.98
K_2SO_4 gypsum	0.62	0.12	0.08	36.43	0.03	45.79	0.02	0.21	0.01	0.01	0.25	16.37	99.93
K_2SO_4 mix	1.75	0.05	0.16	46.66	0.17	33.35	0.02	0.29	0.02	0.02	0.22	17.13	99.84
K_2SO_4 mix	1.65	0.04	0.14	45.41	0.21	32.30	0.02	0.36	0.01	0.02	0.20	19.54	99.90
Na_2SO_4 gypsum	0.53	0.03	0.08	42.04	0.08	45.46	0.03	0.10	0.01	0.01	0.26	11.35	99.98
Na_2SO_4 gypsum	0.16	0.05	0.06	38.00	0.06	48.84	0.03	0.05	0.01	0.00	0.27	12.34	99.86
Na_2SO_4 mix	1.51	0.05	0.15	43.59	0.18	33.14	0.02	0.02	0.01	0.02	0.20	21.01	99.90
Na_2SO_4 mix	1.34	0.03	0.13	43.87	0.16	36.81	0.03	0.03	0.01	0.02	0.22	17.26	99.90
$ZnSO_4.7H_2O$ gypsum	0.35	0.04	0.11	41.29	0.08	53.28	0.01	0.01	0.01	0.01	0.27	4.39	99.83
$ZnSO_4.7H_2O$ gypsum	1.31	0.01	0.12	36.92	0.05	52.35	0.01	0.01	0.01	0.01	0.24	8.87	99.90
$ZnSO_4.7H_2O$ mix	1.31	0.05	0.17	42.90	0.21	29.65	0.02	0.02	0.01	0.02	0.20	25.38	99.93
$ZnSO_4.7H_2O$ mix	1.30	0.04	0.13	39.89	0.20	31.57	0.02	0.02	0.01	0.02	0.19	26.44	99.81
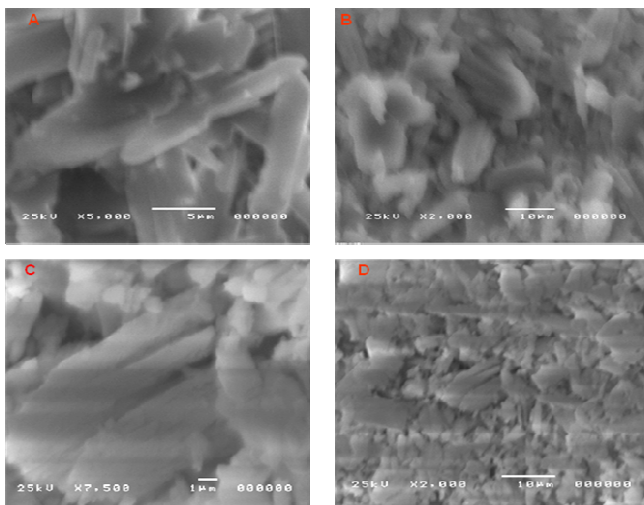
Fig. 7. SEM micrographs of the standard gypsum stucco samples: A & B untreated and non-aged gypsum stucco samples, needle-like crystals relate to gypsum crystals, C & D untreated and aged gypsum stucco samples, the noticeable difference in most of the crystal forms may be related to the transformation to anhydrite as a result of heating at 300ºC ± 10.
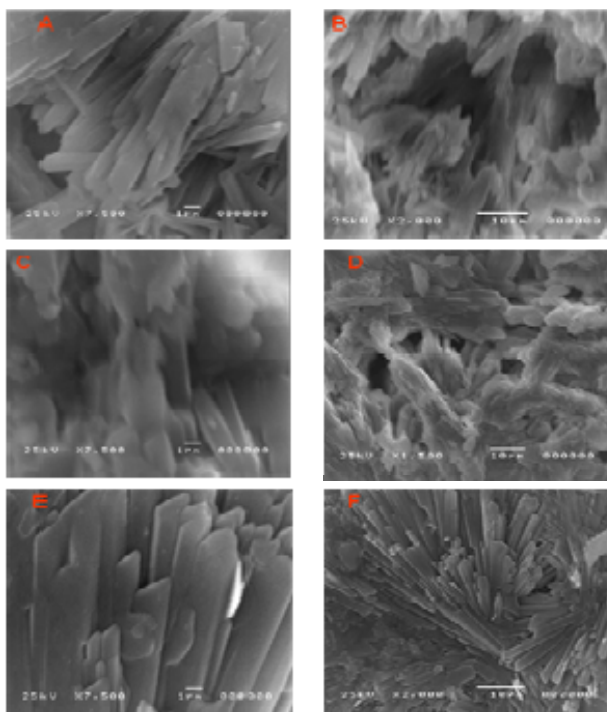

Fig. 8. SEM micrographs of the treated gypsum stucco samples with the selected sulphate activators. A & B, aged gypsum stucco samples after treating with K_2SO_4, the interlocked needle-like crystals relate to the reformation of gypsum crystals, C & D, aged gypsum stucco samples after treating with Na_2SO_4, the interlocked needle like crystals relate to the formation of gypsum crystals, E & F aged gypsum stucco samples after treatment with $ZnSO_4.7H_2O$, again, needle-like crystals relate to the formation of gypsum crystals.
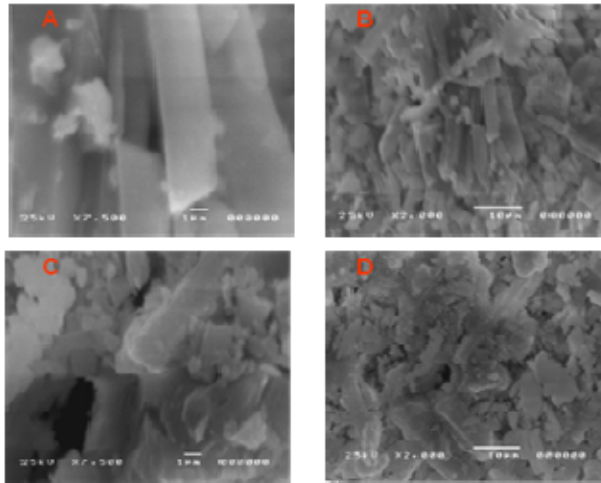
Fig. 9. SEM micrographs of the standard gypsum lime stucco samples: A and B untreated and non-aged gypsum lime stucco samples, needle-like crystals relate to gypsum crystals, C and D untreated and aged gauged stucco samples, the noticeable differences in most of crystal forms may be related to the transformation to anhydrite as a result of heating at $300 \pm 10^{o}C$.
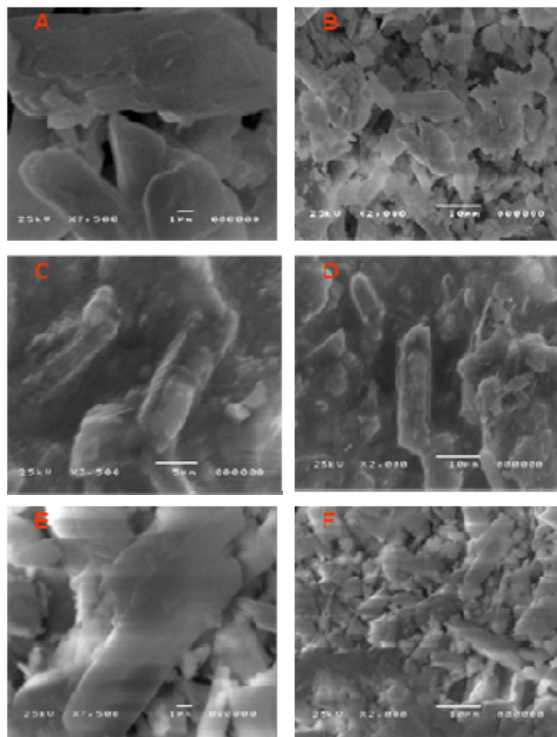

Fig. 10. SEM micrographs of the treated gauged stucco samples with the selected sulphate activators: A and B, aged gauged stucco samples after treating with K_2SO_4, some elongated crystals may be related to the formation of gypsum crystals, C and D, aged gypsum lime stucco samples after treating with Na_2SO_4, something among the elongated gypsum crystals may be related to the reformation sodium chloride crystals as proved by XRD analysis. E & F aged gypsum lime stucco samples after treating with $ZnSO_4 \cdot 7H_2O$; also, some elongated crystals may be related to the formation of gypsum crystals.

Measurement of physical and mechanical properties

All treated stucco samples achieved physical and mechanical properties greater than the aged stucco samples, which may be a result of retransformation of anhydrite to gypsum; all details have been shown in Table 2.

Table 2. Results of some physical and mechanical properties of the standard and the treated stucco samples with the selected sulphate activators.

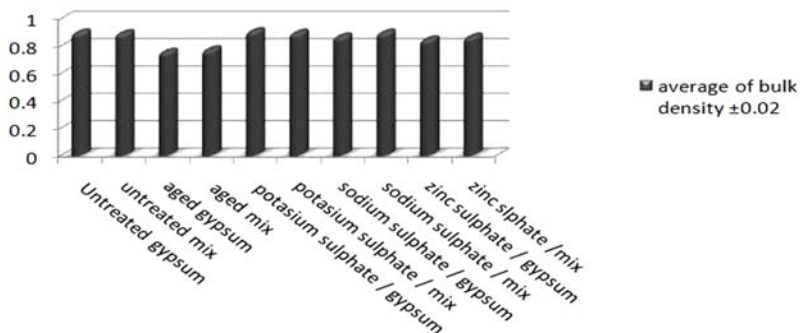| Parameter \ Samples	Gypsum and mixed (gypsum lime) stucco samples
Bulk density	All treated stucco samples achieved bulk density average greater than the aged stucco samples, which may be a result of retransformation of anhydrite to gypsum (Fig. 11)
Water absorption ratio	All treated stucco samples achieved average water absorption less than the aged stucco samples (Fig. 12).
Apparent porosity	All treated stucco samples achieved average of apparent porosity less than the aged stucco samples (Fig. 13).
Compressive strength of dry and wet stucco samples	All treated stucco samples achieved mechanical properties (compressive strength of wet and dry stucco samples) average greater than the aged stucco samples (Figs. 14 and15), especially K_2SO_4 and Na_2SO_4 that may be due to retransformation of anhydrite to gypsum. But the strength increasing ratio in $ZnSO_4 \cdot 7H_2O$ gypsum stucco samples was very low, and that may be related to the non-interlocked gypsum crystals (Fig. 8E and F).

Fig. 11. All stucco samples achieved a bulk density average greater than the aged stucco samples, which may be a result of retransformation of anhydrite to gypsum.
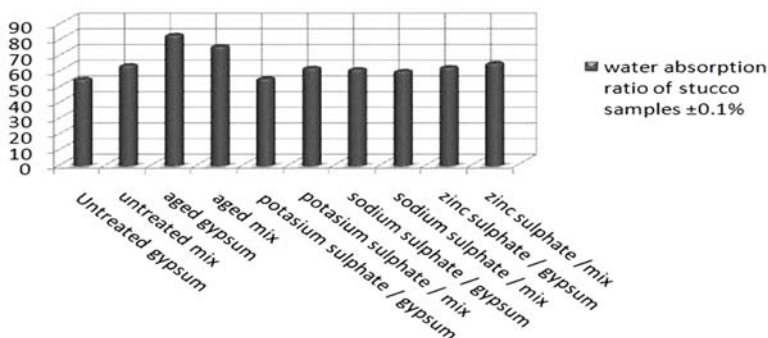

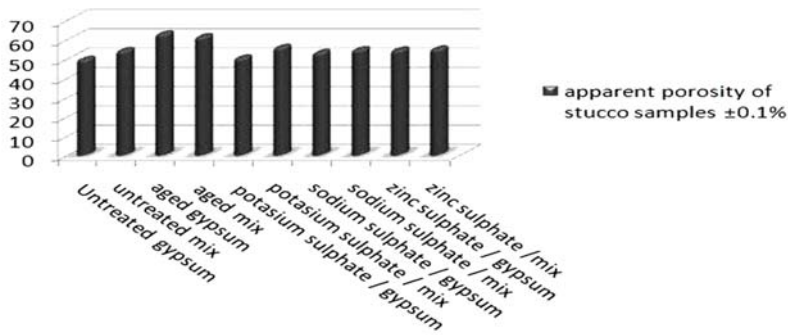**Fig. 12.** All stucco samples achieved average water absorption less than the aged stucco samples.

Fig. 13. All stucco samples achieved average of water absorption and apparent porosity less than the aged stucco samples.
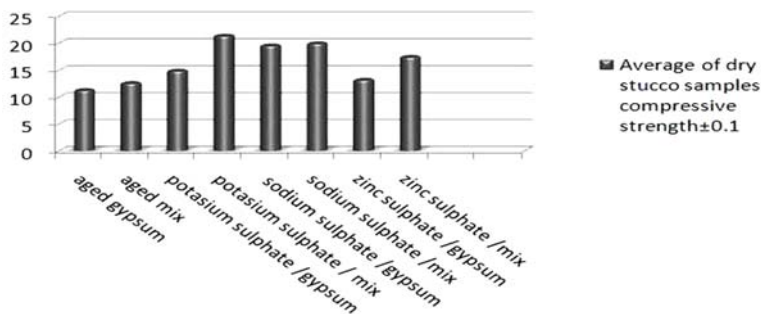

Fig. 14. All stucco samples achieved average of compressive strength of dry stucco samples greater than the aged stucco samples, which may be a result of retransformation of anhydrite to gypsum. The increasing ratio in $ZnSO_4·7H_2O$ gypsum stucco samples was very low, that may be due to the non-interlocked gypsum crystals.
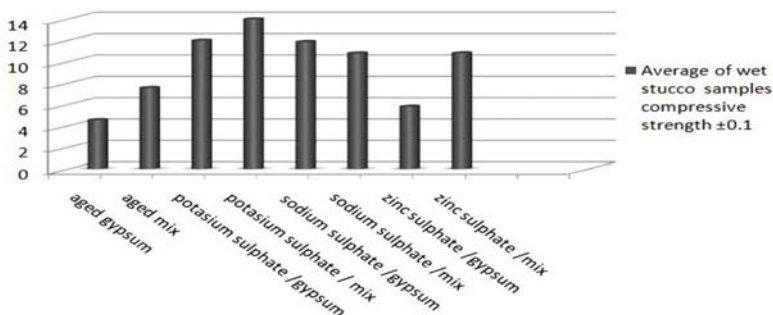

Fig. 15. All stucco samples achieved average of compressive strength of wet stucco samples more than the aged stucco samples, especially K_2SO_4 and Na_2SO_4, which may be a result of retransformation of anhydrite to gypsum. The increasing ratio in $ZnSO_4·7H2O$ gypsum stucco samples was very low, and may relate to the non-interlocked gypsum crystals.

Artificial aging by sodium chloride

The effect of sodium chloride aging cycles on gypsum and gypsum lime treated stucco samples with the selected sulphate activators in comparison with the aged standard samples showed an improvement in the appearance of the treated samples, especially, samples that were

treated with K_2SO_4, but without preventing salt efflorescence; this means that sulphate activators don't close the pores of the samples but decrease them (Fig. 16).
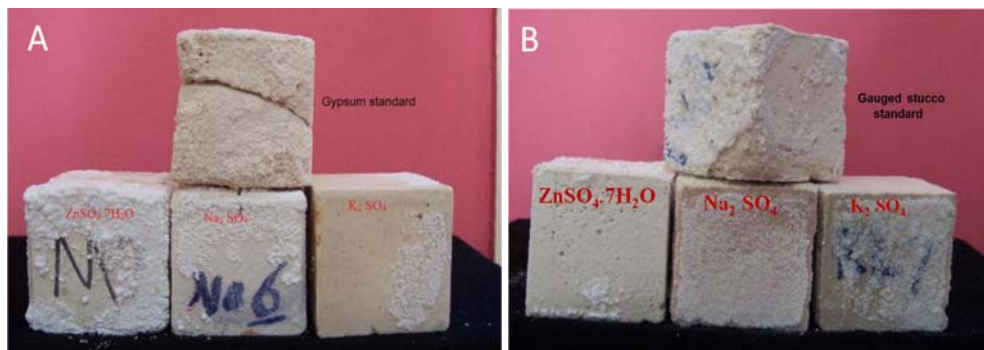

Fig. 16. Photographs show the effect of sodium chloride aging cycles on gypsum and gypsum lime stucco treated samples with the selected sulphate activators in comparison with the aged standard samples.

Conclusion

This work is a response to a question about the possibility of using sulphate activators solutions as a consolidants for the transformed gypsum in archeological stucco, by retransforming anhydrite to gypsum. According to the above results, it is possible to ascertain that sulphate activators can be used in retransforming anhydrite to gypsum. We present the most significant results of the morphological examination and analysis of treated and untreated stucco samples with sulphate activators, which proves the conversion of anhydrite to gypsum. K_2SO_4 activator gave the best results, followed by the Na_2SO_4 activator, although the $ZnSO_4·7H_2O$ activator succeeded in transforming anhydrite, without, however, giving satisfactory mechanical results; this may be related to the shapes of the non-interlocked gypsum crystals. According to the results of chemical analysis, all the elemental oxides related to the use of sulphate activator solutions are still in the range of traces (i.e., do not exceed 0.45%), which decreases the possibility of forming harmful salts or a reaction with other components of the stucco such as calcium carbonate. Finally, we studied the effects caused by sodium chloride as an aging parameter; all treated samples had been affected by the salt but less than the standard samples and the treatments have not closed the pores.

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