

**Deterioration of Limestone and Marble- A Case Study on the Mausoleum of As-Saleh Nagm Ad-DIN Ayyub in Cairo
(Monument no.38) (641-648 A. H. /1243-1250 A.D.).**

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Summary -The mausoleum of As-Saleh Nagm Ad-Din Ayyub in Cairo (Egypt), built with limestone and marble for the portal is heavily weathered, due to damp rising from the ground. The deterioration phenomena affected the building materials were studied and the causes that led to them were determined. In order to achieve this study different analytical techniques were used, including X-ray diffraction, atomic absorption spectroscopy and ion chromatography. Determination of the mobile cations and anions concentrations in the aqueous extractions from selected samples followed by statistical study of the obtained results were carried out to identify the abundant salts. The study proved that, three salts affected the building, produced five deterioration phenomena, and the saline solutions from the ground which transported by rising water are the main source of the formed salts. The results have been reported and discussed.

Introduction

An important part of the historical architectural heritage of Egypt is located in Fatimid Cairo city. The mausoleum of As-Saleh Nagm Ad-Din Ayyub is one from the most important cases in Fatimid Cairo of the severe deterioration by rising damp. May be it is very strange to mention that, the mausoleum was studied and presented in this paper as an important case of limestone and marble deterioration although the Egyptian supreme council of antiquities finished the all restoration and conservation works in it!

The phenomena of deterioration that affected the mausoleum were characterized; they are mainly belonging to the following five typologies:

Scales (Fig. 1), salt efflorescence (Fig. 2), salt sub-efflorescence (Fig. 3) cracking (Fig. 4), and big dark spots of humid aspect (Fig.5). The first four typologies were restricted at height between 1 m and 3 m above ground while the last one appeared restricting at

height between 4 m and 5 m above ground. The present study searched the causes that led to their occurrence and to their above-mentioned distribution.

The information obtained from good observation of the mausoleum especially its main façade was combined with the data obtained from analyses and statistical study to evaluate the contribution of all possible compounds and weathering agents towards the present state of the monument.



Fig. 1. Scales, one of the common superficial detachment forms.



Fig. 2. The concentration of soluble salts present on the wall surface; as efflorescence.



Fig. 3. The concentration of soluble salts present on the wall subsurface; as sub-efflorescence.



Fig. 4. Cracks extend in an irregular way close to the horizontal.



Fig. 5. A common characteristic of the mausoleum and most monuments built in Fatimid Cairo city; the big dark spots of humid aspect.

Experimental

Sampling strategy

A marked development of capillarity rising damp was observed on the main façade of the mausoleum, therefore the sampling strategy depended on division of the façade including the portal of marble horizontally to five zones, the first zone was at 1 m height above the ground level and the distance between every zone was also one meter height. Selected samples were taken from the original stone in the places of scales and dark spots of humid aspect, from the powders present in the cracks and also from the crystallized salts in the form of efflorescence and sub-efflorescence from every zone. The salt samples were scraped off with the edge of small plastic bags and kept in especial closable ice bags to avoid any dehydration because of warmth.⁽⁶⁾

Samples preparation

In order to determine the soluble salts the collected stone and powder samples were ground to be fine powders, and then dispersed in deionized water. The suspensions were filtered over a Millipore filters and the filtrates were analyzed for the ionic content.⁽¹¹⁾ In order to determine the type of salts phases the collected crystallized salts were ground quickly to avoid dehydration using ball mill, sample container and balls made of agate and analyzed by means of X-ray diffraction.

Instrumentation

Atomic absorption spectroscopy (AAS) technique was used to quantify the mobile Ca^{+2} , Mg^{+2} , Na^+ and K^+ cations- in the aqueous extractions using Philips PU 9100 Atomic Absorption Spectrometer. Ion chromatography (IC) was employed for the mobile Cl^- , NO_3^- and SO_4^{-2} anions determinations in the same aqueous extractions using 690 Ion chromatograph from Metrohm equipment with this technical data: Column size 125x4.0 mm, polystyrol/Divinylbenzol-copolymer with Ammonium group quarterner. The data of the used eluent is (2 m mol/l phtalic acid in 10% acetone, pH 5) and the flow rate of it was 2 ml/min., with sensitivity $10 \mu\text{s cm}^{-1}$ and 7.4 bar for pressure. X-ray diffraction was employed for determination the type of phases composing the salts using equipment Philips PW 1729 X-ray diffractometer under the following conditions: $\text{CuK}\alpha$ radiation (1.5418\AA) with 30 kV, 30 mA energy and graphite Monochromator, the XRD instrument provided with computerized system with ADM computer program for measurement and evaluation.

Results and Discussion

1. Stone Samples

Table 1 shows the results obtained from the chemical analyses of the aqueous extractions from the stone and powder samples. Concentrations of ions are expressed in weight percent. It was found that, Ca^{+2} is the main cation, and Cl^- , NO_3^- and SO_4^{-2} are the most important anions and of the highest concentration values.

Origin of the ions

The high concentrations of Ca^{+2} are due to the calcite which the essential mineral in both limestone and marble; the original building materials in the studied mausoleum. The present work suggests that, Ca^{+2} was partially dissolved and leached out from the calcite by the absorbed water inside the stone and the presence of SO_4^{-2} in this water increased the leaching process of it. Ground waters in soil are more or less diluted salt solutions. They contain carbonate, sulphate, chloride, nitrate,

magnesium, calcium, sodium, potassium and ammonium ions. Compared to the normal soil solutions, those present near human housings and sites (as in this studied case) are enriched in nitrate and chloride, nitrate being produced by micro organisms from organic refutes, and chlorides being supplied by the consumption of sodium chloride.⁽⁹⁾ An additional source of SO_4^{-2} accumulation is the polluted atmosphere.^(1, 12 and 15)

Behavior of the ions

The results revealed that, the concentrations of SO_4^{-2} are very high in the first three zones and very low in the last two zones namely zones D and E which affected by the big dark spots of humid aspect, in the opposite of the behavior of both Cl^- and NO_3^- which their concentrations are very low in the first three zones and very high in the last two zones as shown in (Fig. 6).

This can be explained as follows: the water evaporates and the solutes concentrate, and the different salt phases will precipitate in sequences according to their solubilities when and where the solution becomes supersaturated.⁽⁸⁾ Thus, as shown in (Fig. 6); the less soluble sulphate is concentrated and enriched in the lower zones and the more soluble nitrate and chloride in the upper zones.

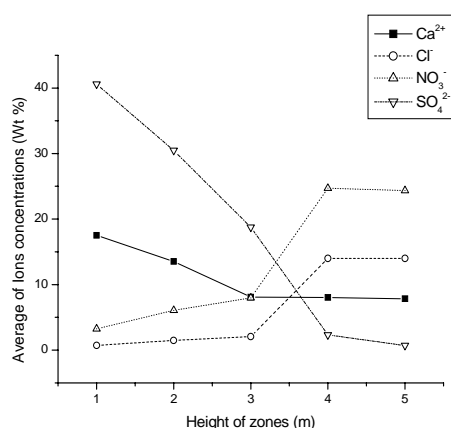


Fig. 6. Distribution of Ca^{+2} , Cl^- , NO_3^- and SO_4^{-2} ions in relation to height on the façade of the mausoleum

Table 1. Results of IC and AAS analyses on the aqueous extractions from the stone and powder samples (concentrations expressed in wt %)

Zone	Sample	Deterioration typology	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
A	L1	Scales	13.73	0.71	0.19	0.11	1.35	3.99	33.11
	L2	Scales	15.09	0.89	0.15	0.07	0.63	2.57	33.73
	L3	Cracking	17.33	1.03	0.23	0.17	0.31	2.83	39.09
	M4	Cracking	18.93	0.95	0.41	0.19	0.49	2.91	43.11
	M5	Scales	17.75	1.31	0.27	0.13	1.11	4.61	41.05
	M6	Cracking	19.67	0.29	0.17	0.09	0.91	3.05	45.97
	L7	Scales	20.11	1.87	0.13	0.13	0.27	2.81	48.06
B	L8	Scales	12.81	1.05	0.49	0.21	1.71	5.09	29.05
	L9	Cracking	11.05	1.15	0.58	0.19	1.93	6.73	23.11
	L10	Scales	13.73	1.13	0.51	0.25	0.95	5.91	31.71
	M11	Cracking	12.85	0.87	0.73	0.17	2.07	6.03	27.93
	M12	Cracking	15.13	1.07	0.39	0.23	1.77	6.81	35.55
	M13	Scales	17.15	0.91	0.91	0.11	0.89	5.71	37.61
	L14	Cracking	11.99	0.79	0.63	0.29	1.03	6.11	28.33
C	L15	Cracking	8.81	0.33	0.67	0.41	1.87	6.99	19.01
	L16	Scales	7.37	1.09	0.75	0.49	2.17	8.03	15.97
	L17	Scales	6.99	0.75	0.69	0.61	2.61	7.69	16.64
	L18	Cracking	9.07	0.51	0.87	0.53	1.97	8.13	21.59
	L19	Scales	8.25	1.03	0.57	0.71	1.47	7.79	19.64
	L20	Scales	6.89	0.29	0.73	0.47	2.11	8.17	16.40
	L21	Scales	9.27	0.31	0.47	0.59	2.31	9.01	22.06
D	L22	Humid spot	8.17	0.63	0.89	0.77	13.63	25.31	1.77
	L23	Humid spot	8.05	0.81	0.79	0.97	13.77	24.59	2.03
	L24	Humid spot	9.03	0.21	0.91	0.73	15.97	27.13	2.07
	L25	Humid spot	6.97	0.33	0.95	0.87	12.75	21.07	4.91
	L26	Humid spot	7.81	0.23	1.03	0.95	13.97	24.55	1.37
	L27	Humid spot	9.01	0.41	0.97	0.87	14.93	28.09	1.87
	L28	Humid spot	7.19	0.27	0.77	0.79	13.01	22.25	2.21
E	L29	Humid spot	8.17	0.27	1.07	0.89	14.07	26.05	0.51
	L30	Humid spot	9.31	0.17	0.69	0.95	16.61	28.81	0.79
	L31	Humid spot	7.91	0.13	0.95	1.09	14.71	24.47	0.97
	L32	Humid spot	6.09	0.15	1.09	0.97	10.91	18.84	0.91
	L33	Humid spot	7.37	0.13	1.13	1.05	13.15	22.80	0.39
	L34	Humid spot	8.01	0.17	1.17	0.99	14.19	24.78	0.53
	L35	Humid spot	7.97	0.23	1.21	1.13	14.37	24.66	0.81

L: Limestone

M: Marble

The statistical study of the ions values

The correlation coefficients were calculated between the ions values; the matrices can be shown in table 2. The obtained results can be summarized as follows: strong linear correlation coefficients ($R = 0.982$, $R = 0.966$ and $R = 0.938$) associated with the equations $SO_4^{2-} = 2.3721 Ca^{+2} - 0.9603$, $SO_4^{2-} = 2.3216 Ca^{+2} - 0.9411$ and $SO_4^{2-} = 2.3357 Ca^{+2} - 0.1455$ were obtained between the Ca^{+2} ion values on one hand and the SO_4^{2-} ion values on the other hand in the aqueous extractions from the samples of zones A, B and C respectively. Besides, these equations are very similar to the $SO_4^{2-} = 2.3967 Ca^{+2}$ equation of gypsum. Basically this means that, all Ca^{+2} ions combine with SO_4^{2-} ions crystallizing as gypsum during water evaporation; while their values of zones D and E did not allow good correlations as shown in (Fig. 7).

Table 2. Correlation coefficient matrices obtained for the measured cations and anions (strong R indicated in bold).

		Ca^{2+}	Mg^{2+}	Na^+	K^+
Zone A	Cl^-	-0.527	-0.476	-0.042	-0.430
	NO_3^-	-0.263	0.020	0.172	-0.016
	SO_4^{2-}	0.982	0.330	0.076	0.301
Zone B	Cl^-	-0.447	0.241	-0.321	-0.142
	NO_3^-	-0.153	0.223	-0.264	0.173
	SO_4^{2-}	0.966	-0.127	0.185	-0.282
Zone C	Cl^-	-0.356	-0.200	0.047	-0.153
	NO_3^-	0.184	-0.163	-0.312	0.301
	SO_4^{2-}	0.938	-0.360	-0.304	0.271
Zone D	Cl^-	0.928	-0.214	0.278	-0.303
	NO_3^-	0.986	0.079	0.274	-0.167
	SO_4^{2-}	-0.570	-0.130	0.036	-0.010
Zone E	Cl^-	0.982	0.177	-0.613	0.025
	NO_3^-	0.996	0.369	-0.564	-0.179
	SO_4^{2-}	-0.114	-0.214	-0.348	0.309

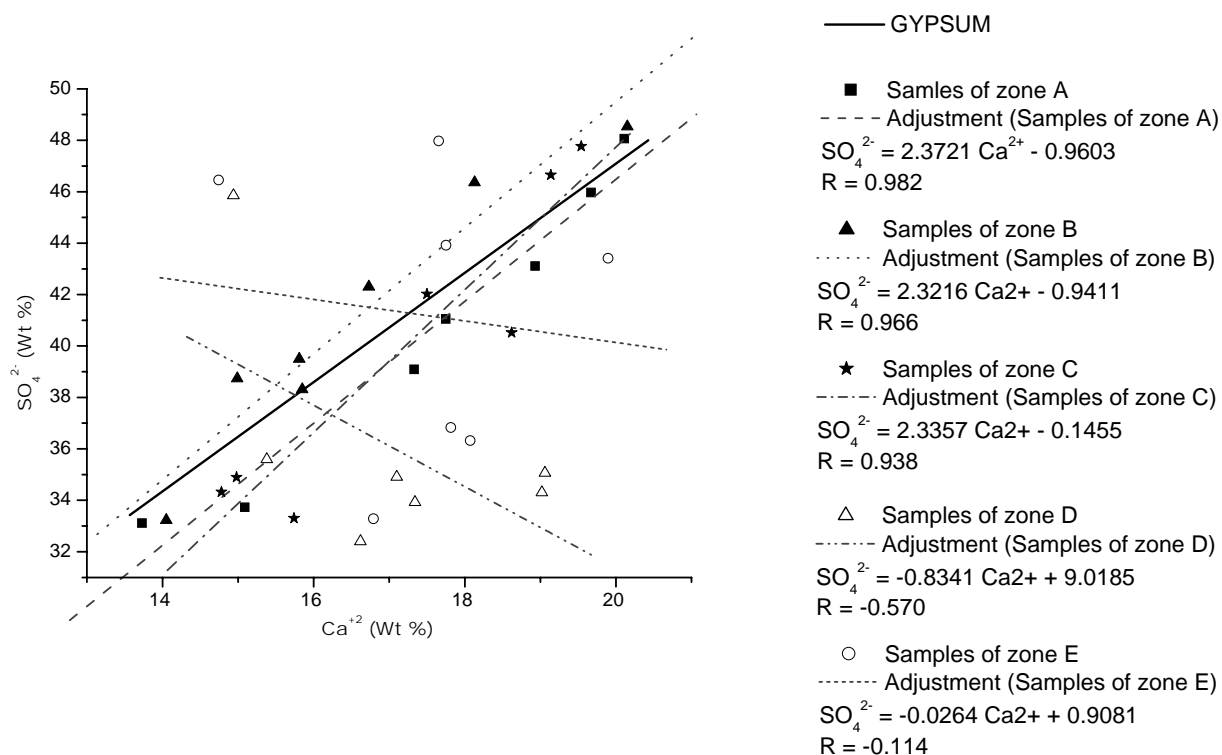


Fig. 7. Statistical correlation between the Ca^{2+} and SO_4^{2-} values of the chemical analyses carried out in the aqueous extractions from stone samples of five zones.

Concerning the Ca^{+2} and the Cl^- values in zones A, B and C, they did not allow good correlations; while strong linear correlation coefficients ($R = 0.928$ and $R = 0.982$) were obtained between their values in zones D and E associated with the equations $Cl^- = 1.294 Ca^{+2} + 3.6104$ and $Cl^- = 1.7484 Ca^{+2} + 0.3068$ respectively. Besides, these equations are very similar to the $Cl^- = 1.7691 Ca^{+2}$ equation of antarcticite as shown in (Fig. 8).

Concerning the Ca^{+2} and the NO_3^- values in zones A, B and C, they did not also allow good correlations; while their values in zones D and E allowed strong linear correlations ($R=0.986$ and $R=0.996$) associated with the equations $NO_3^- = 3.0528 Ca^{+2} + 0.1898$ and $NO_3^- = 3.1404 Ca^{+2} - 0.2535$ respectively. Besides, these equations are very similar to the $NO_3^- = 3.0940 Ca^{+2}$ equation of nitrocalcite as shown in (Fig. 9).

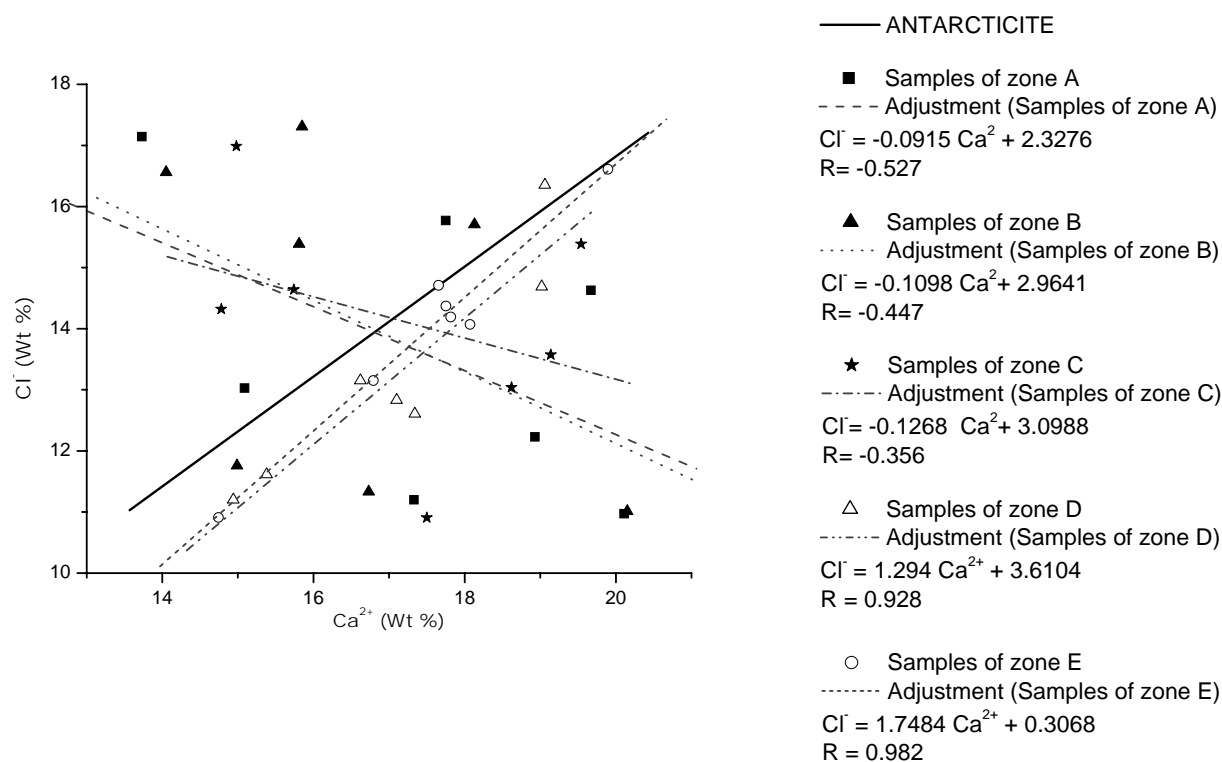


Fig. 8: Statistical correlation between the Ca^{2+} and Cl^- values of the chemical analyses carried out in the aqueous extractions from stone samples of five zones.

It was observed that, the broad occurrence of gypsum in the efflorescence form and this corresponds with what was mentioned in literature⁽¹⁵⁾, and also in the sub-efflorescence form as shown in (Figs. 2 and 3) respectively.

All soluble salts occur at least in the most places where deterioration occurs,⁽²⁾ they may produce very strong decay⁽⁷⁾, and provoke the alteration of the blocks by detachment and exfoliation etc.⁽¹⁶⁾ Therefore the present study attributes both scales and cracking phenomena affected the façade of the mausoleum to gypsum formation in sub-efflorescence form and this corresponds with literature⁽¹⁰⁾ which attributed plaques phenomenon which is similar to scales to gypsum occurrence because the crystallization of it and its recrystallization from a lower to a higher hydrate within the range of mineral stability may develop stresses of high magnitude.^(13, 14)

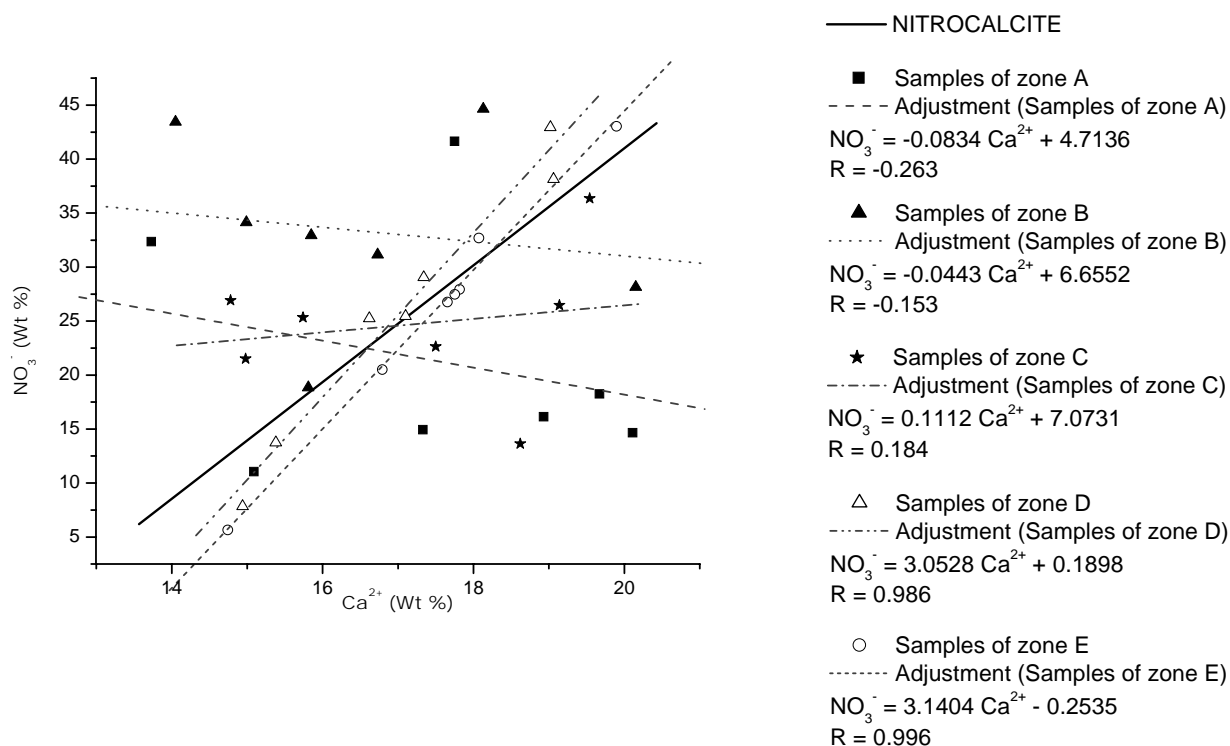


Fig. 9: Statistical correlation between the Ca^{2+} and NO_3^- values of the chemical analyses carried out in the aqueous extractions from stone samples of five zones.

2. Salt Samples

X-ray diffraction analysis of the taken samples from the first three zones A, B and C proved the presence of gypsum salt as shown in (Fig. 10).

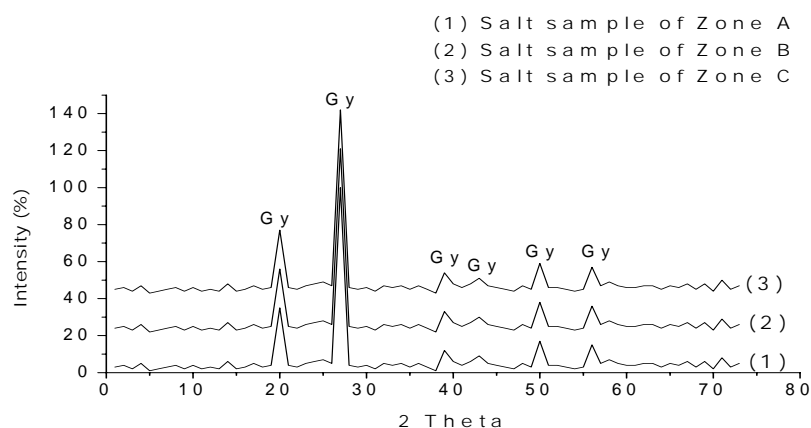


Fig. 10. X-ray diffraction patterns of salt samples taken from the first three zones

It was observed that, no crystallized salts were found in both zones D and E although the chemical analyses using IC and AAS followed by the statistical study

proved the presence of both antarcticite and nitrocalcite. How can one explain this? The chloride and nitrate of Ca^{2+} form very hygroscopic salts.⁽⁵⁾ These hygroscopic salts can absorb moisture from the ambient humid air, when the relative humidity is higher than the equilibrium relative humidity of the saturated solution.⁽⁴⁾ So the salts will dissolve and the wall in contact with the salt solutions gets moist. Antarcticite does that at relative humidity above 30% and nitrocalcite at relative humidity above about 55%.⁽⁵⁾ This means that antarcticite cannot crystallize under normal conditions on walls.⁽³⁾ The present study confirms that, the relative humidity around the mausoleum is very high because of the continuous supply of rising damp from the ground; therefore the study attributes the big dark spots of humid aspect phenomenon affected the two highest zones D and E to this behavior of these two hygroscopic salts. This also explains; why are these two higher zones more humid than the three lower zones.

Conclusion

The first step of restoration and conservation of the mausoleum is to stop rising damp on walls from the ground, and then the beginning of consolidation process for the decayed basis by injection with suitable consolidants will be the second step, and so on with the rest of restoration and conservation procedures. If the recommended first step is not achieved perfectly, the all restoration and conservation processes will be useless and this is what has been already taken place in the mausoleum. The recommended steps for the studied mausoleum conservation can be applied to all archaeological buildings in Fatimid Cairo city.

Gypsum occurrence is responsible for both scales and cracking phenomena, while antarcticite and nitrocalcite existence in the walls are responsible for the big dark spots of humid aspect phenomena.

References

1. Amoroso, G. and Fassina, V., Stone decay and conservation: Atmospheric pollution, cleaning, consolidation and protection. Elsevier, Amsterdam, pp **453**, (1983).
2. Arnold, A., Behaviour of some soluble salts in stone deterioration. - In: 2nd International. Symposium on the deterioration of building stones, Athens, pp. **27-36**, (1976).
3. Arnold, A., Nature and reactions of saline minerals in walls. – In: The international symposium on the conservation of stone II, Bologna, pp.**13-23**, (1981).
4. Arnold, A., Salzmineralen in mauerwerken, Schweiz. Mineral. Petrogr. Mitt., **147-166**, 61 (1981).
5. Arnold, A. Rising damp and saline minerals. - In: 4th congress on the deterioration and preservation of stone object. Ed. K. Gauri and J. Gwinn, university of Louisville, Kentucky, pp. **11-28**, (1982).
6. Arnold, A., Determination of mineral salts from monuments. - In: Studies in conservation, pp. **129-138**, 29 (1984).
7. Arnold, A. and Kueng, A., Crystallization and habits of salt efflorescences on walls. –In: 5th international congress on deterioration and conservation of stone, Lausanne. Ed. Felix, G., pp. **255-267**, (1985).
8. Arnold, A. and Zehnder, K., Decay of stone materials by salts on humid atmosphere. – In: The VIth international congress on deterioration and conservation of stone, Torun, pp.**138-148**, (1988).
9. Arnold, A. and Zehnder, K., Salt weathering on monuments. – In: The 1st international symposium on the conservation of monuments in the Mediterranean basin, Bari, pp. **31-58**, (1989).
10. Silva, B., Rivas, T., Prieto, B. and Delgado Rodrigues, J., A comparison of the mechanisms of plaque formation and sand disintegration in granite in historical buildings. - In: Degradation and conservation of granitic rocks in monuments. Proc. of EC workshop, Spain, November 1994, Ed. Vicente, M.A. et al., pp. **28- 30**, (1996).

11. Torfs, K., Van Grieken, R., Zezza, F., Garcia, N. and Macri, F., The cathedral of Bari, Italy: Evaluation of environmental effects on stone decay phenomena. – In: Studies in conservation, pp. **193-206**, 42 (1997).
12. Winkler, E.M., Stone in architecture. Properties and durability. Springer-Verlag, Berlin, pp **313**, (1994).
- Winkler, E.M. and Singer, PC., Crystallization pressure of salts in stone and concrete. Geol Soc Am Bull, **3509-3514**, 83(11) (1972).
13. Winkler, E.M. and Wilhelm, EJ., Salt burst by hydration pressures in architectural stone in urban atmosphere. Geol Soc Am Bull, pp. **567-572**, 81(2) (1970).
14. Zehnder, K., New aspect of decay caused by crystallization of gypsum. – In: Conservation of stone and other materials. Ed. Thiel, M. J., London, E and FN: Spon, pp. **107-114**, (1993).
15. Zezza, F., Nuria Garcia Pascua and Fabio Macri, Rising damp and soluble salts in the weathering processes of biocalcarenes. Case study of cathedrals, churches and buildings of Lecce baroque.–In: The LCP congress on preservation and restoration of cultural heritage, Montreux, pp. **161-174**, (1995).