CHEMICAL DETERIORATION OF EGYPTIAN LIMESTONE AFFECTED BY SALINE WATER

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Abstract

Salt forms are aggressive deterioration problems, which occur on all stone surfaces, mortars and renderings through saline solutions transferred to the stone pores. Deterioration of Egyptian limestone is primarily due to water-soluble salts. The formation of these salts on calcareous stone is the most important chemical reaction involving saline water to cause stone degradation. The study explains the different deterioration phenomena and alteration mechanisms that lead to the formation of salt crusts on archaeological limestone surfaces. A simulation laboratory conditions has been created to correspond to the aggressive deterioration environments dominating in most archaeological sites in Egypt. Different scientific instruments such as EDX attached with SEM, XRD, AAS, and ISE have been used to study and evaluate the chemical and mineralogical components of salt crusts and to assess the major ions accumulated within the stone pores. The results show that there are aggressive forms of salt affecting the weathered samples; especially those subjected to Na_2SO_4 followed by samples exposed to 1:1 NaCl and Na_2SO_4. The high level of Cl^- and SO_4^- concentrations found on the decayed stone surfaces gives an accurate evidence of salt migration. The degradation phenomena resulted from salty decay actions has occurred directly through complex mechanisms depending on certain specific factors. These factors such as mineralogical composition of stones, major deterioration factors responsible for the natural variety in stone reactivity and adsorption of some salty ions as Cl^- and SO_4^-. Thereafter production of gypsum, halite and other species of salty crusts, in addition to the dominated environmental conditions.

Keywords: inherent; salinity; crusts; efflorescence; weathering.

Introduction

The decay of building stones is often compared to the effects of an illness most commonly a cancer-undermining the health of a building and eventually leading to its demise [1]. Weathering processes of natural stones depend on their chemical and morphological properties [2]. The deterioration of stone in Egypt is primarily due to several types of water-soluble salts such as halite [3]. Salt crystallization in porous materials constitutes one of the most frequent causes of decay [4] and degradation of buildings, in a wide range of environments [5]. These salts can be observed directly as efflorescence and appear and disappear periodically according to the presence or absence of moisture sources [6]. Pressures created by crystallization of salt in pores weaken the material until its mechanical strength is overcome and damage occurs. Inhibiting or limiting the crystallization of the salt would therefore prevent or slow down the material decay [7]. This problem represents aggressive deterioration forms that take place on all stone surfaces, mortars and renderings through salinity

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solutions that are transferred to the stone pores [8]. This may be understood from the salt concentration that can be defined as a consequence of repeated dissolution and crystallization process [9]. When water evaporates, the salt will deposit either on stone surfaces "efflorescence", beneath the surfaces "sub- efflorescence" or within the pore of the stone itself "crypto efflorescence" [10], especially with repeated wetting and drying cycles which finally lead to stone deformation [11]. The formation of salt crusts on calcareous stone is the most important chemical reaction involving salinity ground water to cause stone degradation. When these crusts are formed on a porous stone, it disintegrates to a powdered material, while limestone and marble develop thick crusts instead [12]. Furthermore, they are formed when calcite in calcite-cemented sandstone, limestone and marble react with different oxides in the presence of moisture sources through several kinds of chemical reactions. This reaction increases when NO_2 is present, probably because NO_2 acts as a catalyst especially for the oxidation of SO_2 to SO_3 on the stone surface [13]. In addition to some other catalytic agents or inherent materials as $Fe^{(2, 3)+}$ and $Mn^{(2, 3)+}$ [14], which play an important role in deterioration process such as sulfation mechanisms which convert carbonates into sulphates (gypsum) [15]. In Egypt, the salt weathering is the main damage process affecting archaeological building materials through aggressive effects caused by some families of salts such as Na_2SO_4, $NaCl$, KNO_3 and KCl etc. (Fig. 1- a and b). Several researches have focused on the reactions between different types of stones and the previous families of salts [16, 17].
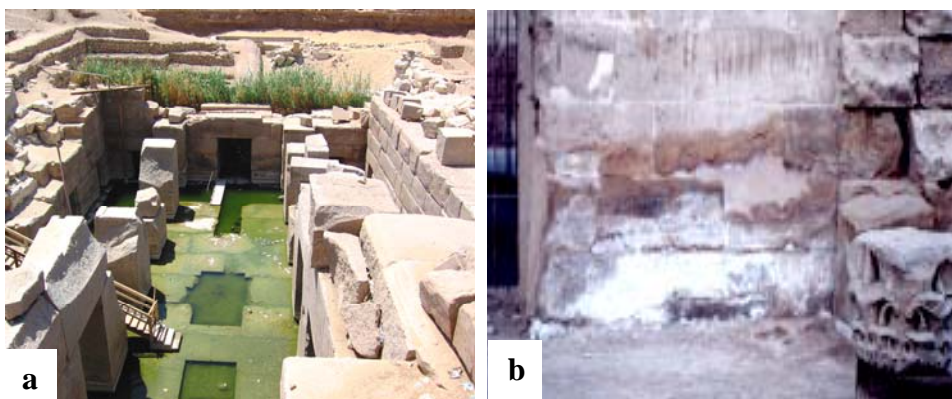
Fig. 1. Images of temples: a - Osirion of Abydos Temple; b - Entrance of Esna Temple

Laboratory Tests and Scientific Investigations

The knowledge about weathering processes is derived essentially from experimental approaches based on laboratory simulation of this phenomenon, where simulation experiments give consideration to the relationship between the durability index and artificial conditions [18]. So, the simulation tests may be useful to confirm the role of alternation process out of which the results obtained [19].

a. Materials and sampling conditions

Several types of samples required for laboratory tests and investigations were prepared, fresh samples of limestone that are used as models for simulation samples were prepared as cubic 3×3×3cm; the first 1mm of the surface was discarded to avoid contamination features. Small fragments of stone were removed from the underside or back of the sculpture SEM observation. Scratched samples were taken for chemical and mineralogical qualitatively and quantitatively analysis by EDX, AAS and ISE (Ion Selective Electrode), in addition to XRD.

b. Laboratory Weathering Cycles.

40 limestone samples were divided into 4 categories; each category contains 10 samples in addition to another one used as a reference category. These categories were submitted to consequently three stages of *artificial weathering cycles* (AWC) which were divided as follows:

- **1st stage** (*slightly weathering cycles*) composed of 12 AWC with total time 288 h. (126 h soaking in salty bath, 36 h in room temperature and 126 h in electric oven 60°C).
- **2nd stage** (*moderately weathering cycles*) composed of 24 AWC with total time 576 h with the same previous procedures (252 h soaking in salty bath, 72 h in room temperature and 252 h in electric oven 60°C).
- **3rd stage** (*heavy weathering cycles*) it was done through other 12 AWC with total time 864 h with the same procedures. (378 h soaking in salty bath, 108 h in room temperature and 378 h in electric oven 60°C). The salinity bathes used with these categories are consequently containing different types of salts as shown in Table 1.

**Table 1.** The chemical composition of different salinity bathes

Category	Salinity Bath Components
1	20 % Na_2SO_4
2	(1:1) of 20 % Na_2SO_4 and 20 % NaCl
3	(1:1:0.5) of 20 % Na_2SO_4, 20 % NaCl and 10 % $FeCl_2$
4	(1:1:0.5) of 20 % Na_2SO_4, 20 % NaCl and 10 % KNO_3

Evaluation Procedures and Results

Several results were proved through different investigation techniques, tools and computer programs, which could be summarized as follows:

a. Results of Elemental Analysis by SEM-EDX

Salt crystallization in the specimens was studied by FEI-SEM equipped with an Energy Dispersive X-ray System (EDX). This technique was mainly used to define the elemental ratios of affected and non affected samples. The results reveal that there are several harmful components which affected the substrate of the samples through some aggressive kinds of salts. All results are listed in Table 2 and Fig. 2-a, b, c and d.
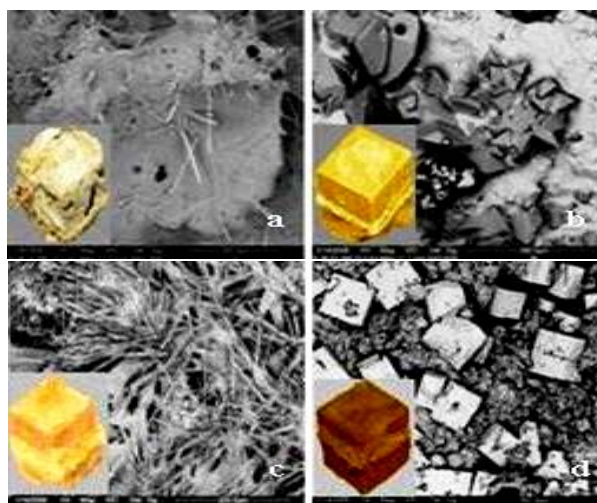
Fig. **2**. Photo and SEM photo-micrographs of affected samples show some types of salts affected the investigated samples: a - Anhydrite, Epsomite, Thenardite (400X); b - Thenardite, Halite, Gypsum (400X); c - Gypsum, Kieserite, Thenardite (500X), d - Mirabillite, Sylvie, Thenardite (200X).

Table 2. EDX analytical results of affected and non-affected samples

Elements	Investigated Category				
	Ref. sample	Cat A*	Cat B***	Cat C**	Cat D***
C	18.17	04.49	07.65	04.16	00.00
O	45.72	28.77	01.82	16.01	01.10
Na	01.86	41.08	44.55	37.70	48.00
Mg	06.37	01.50	01.29	01.75	02.32
K	00.02	00.53	00.62	01.62	05.29
S	00.00	22.10	01.46	09.17	01.45
Cl	00.00	00.20	41.06	26.54	41.00
Ca	27.87	01.34	01.55	3.05	00.84
Total	100.01	100.01	100.00	100.00	100.00

Defined after 1ˢᵗ Stage   **Defined after 2ⁿᵈ Stage*   ***Defined after 3ʳᵈ Stage*

b. Results of Bulk Elemental Analysis by AAS and Ion Selective Electrode

Atomic Absorption Spectroscopy (AAS) and Ion Selective Electrode (ISE) analytical methods were performed to identify the soluble salts affecting the stone crusts and to evaluate their different components "cations and anions" the investigations results are shown in Table 3.

Table 3. Chemical analytical results of water soluble fraction of affected samples

Analytical Results mg/l		Ref. sample	Cat D***		Cat C**		Cat B***		Cat A*	
			mg/l	%	mg/l	%	mg/l	%	mg/l	%
Cations (AAS)	Na^+	Distilled Water	12.52	49.39	14.98	45.20	9.50	53.51	10.24	28.71
	K^+		0.14	0.53	0.13	0.50	0.13	0.73	4.09	11.46
	Ca^{++}		10.37	40.90	15.26	46.04	6.41	36.13	19.79	55.49
	Mg^{++}		1.21	4.79	1.50	4.50	0.50	2.74	0.59	1.65
	Fe^{++}		1.11	4.39	1.30	3.88	1.22	6.89	0.96	2.69
Anions (ISE)	HCO_3^-		0.37	1.74	0.402	1.750	0.27	1.33	1.02	4.50
	Cl^-		0.59	2.75	12.08	53.95	4.93	24.10	8.16	35.92
	SO_4^{2-}		20.52	95.37	9.85	44.28	15.23	74.49	13.20	58.12
	NO_3^-		0.03	0.14	0.01	0.04	0.02	0.08	0.332	1.46

Defined after 1ˢᵗ Stage   **Defined after 2ⁿᵈ Stage*   ***Defined after 3ʳᵈ Stage*

c. Results of Mineralogical Analysis by XRD

Mineralogical investigations were done by XRD for defining the different crystalline phases of samples and analyzing the bulk stone composition before and after weathering cycles. The results prove that there are great differences between the weathering products according to the quality and quantity of inherent materials dominated in the groundwater, all results are shown in Table 4.

Table 4. The analytical results "*qualitative and semi-quantitative*" of affected samples

	Minerals	Chemical Composition	Changing % in the mineralogical Composition in Different Categories				
			Ref.	A*	B***	C**	D***
Essential	*Calcite*	$CaCO_3$	69.44	31.17	24.52	45.55	33.76
	Dolomite	$CaMg(CO_3)_2$	04.71	-	-	-	-
	Montmorillonite	$Na\text{-}Al\text{-}Mg\text{-}Si\text{-}O\text{-}OH\text{-}H_2O$	13.56	0.65	-	-	-
	Phillipsite	$KNaCaFeAlSiO_6 \cdot 39H_2O$	03.91	-	02.54	-	-
Salts and Weathering Products	*Anhydrite*	$CaSO_4$	-	05.71	-	1.14	-
	Bischofite	$MgCl_2 \cdot 6H_2O$	-	-	02.42	-	1.10
	Epsomite	$MgSO_4 \cdot 7H_2O$	-	08.18	06.26	4.65	5.49
	Gypsum	$CaSO_4 \cdot 2H_2O$	08.36	14.42	11.38	6.61	4.07
	Halite	$NaCl$	-	-	30.81	13.55	12.99
	Kieserite	$MgSO_4 \cdot H_2O$	-	05.39	03.15	5.55	3.66
	Mirabillite	$Na_2SO_4 \cdot 10H_2O$	-	08.12	03.33	4.33	19.76
	Natrite	Na_2CO_3	-	01.69	-	-	3.55
	Nitratine	$NaNO_3$	-	-	-	-	3.17
	Siderite	$FeCO_3$	-	-	-	2.78	-
	Sylvite	KCl	-	-	05.21	1.80	3.91
	Thenardite	Na_2SO_4	-	23.38	10.35	8.73	8.55
	Thermonatrite	$Na_2CO_3 \cdot H_2O$	-	01.30	-	5.31	-
	Total %		99.99	100.0	99.96	99.99	100.0

Defined after 1ˢᵗ Stage   **Defined after 2ⁿᵈ Stage*   ***Defined after 3ʳᵈ Stage*

Discussions

Formation and distribution of salts on stone surfaces is essentially depend on several variables such as kind and concentration of salt soluble in the ground water, in addition to the kind of stone itself. Moreover, the alternation effects between wetting and drying cycles, and the hydration and the crystallization pressures as essential processes of masonry deterioration [20] [21]. In the present study, the weathering state of stones can be described through a number of chemical characteristics variations. Through evaluating the results of these examinations, it could be decided that the processes of salt formation are highly remarkable in the samples treated by Na_2SO_4 followed by the samples contaminated by 1:1:0.5 of Na_2SO_4, NaCl and $FeCl_2$ that also affected visually by red color. This color which essentially owing to the effect of Fe^{2+} ion, followed by the samples contaminated by 1:1 of Na_2SO_4 and NaCl salts. Finally the samples exposed to effects of 1:1:0.5 Na_2SO_4, NaCl and KNO_3 as source of salts.

Chemically, evaluating the EDX data presented in Table 2 reveals that there are high variations between the elements responsible for the increase of salty weathering comparing with the standard one. On the one hand, **Na**% was 41.08 in 1st category, 44.55 in 2nd category, 37.70 in 3rd one and 48.00 in 4th category (Fig 3-a). **S**% frequently was of salty weathering comparing with the standard one. Where it is 22.10 in 1st category, 01.46 in 2nd category, 09.17 in 3rd one and 01.45 in 4th category (Fig 3-b). On the other hand, the **Cl**% is 00.20 in 1st category, 41.06 in 2nd category, 26.54 in 3rd category and 41.00 in 4th category (Fig 3-c). Finally **Ca** as a main source of limestone samples is decreasing in all weathered samples compared with the standard one as follows 1st category contains 27.87%, 2nd one 01.34%, 3rd category 3.05% and 0.84% in 4th category (Fig 3-d). These variations may have been due to the quantity of salt in weathering paths themselves, or due to the ions exchange between the main components of stone samples and different salty ions present in the solutions.
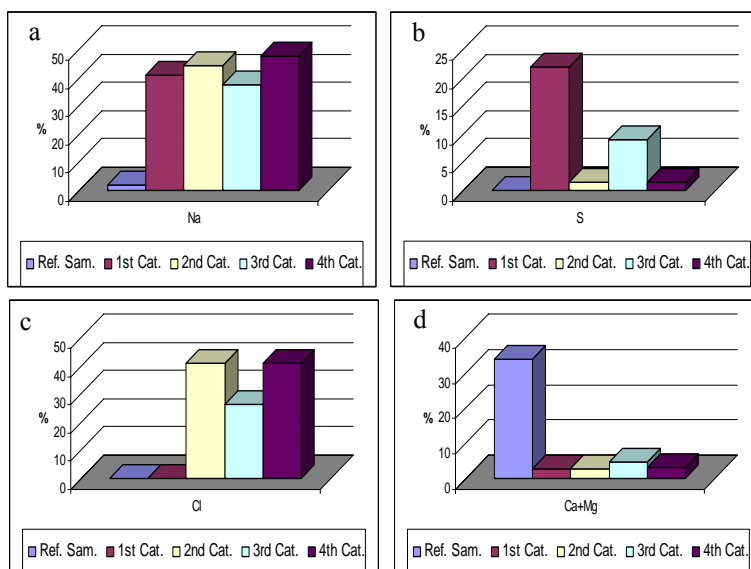

Fig. 3. EDAX analytical results of affected samples compared with standard sample

AAS and titration analytical methods presented in Table 3 show that all investigated samples were aggressively affected by salinity weathering cycles composing the main elements of salts. Where the 1st category characterizes by the presence of the main components both of sulfides and haloids (49.39% Na^+, 40.904% Ca^{2+}, 4.785% Mg^{2+} and 4.394% Fe^{2+} as cations, and 95.368% SO_4^{2-}, 2.753% Cl^- and 1.740% HCO_3^- as anions). Within the same context, the 2nd

category contains the same components with increasing the source of haloids (45.200% Na^+, 46.036% Ca^{2+}, and 4.500% Mg^{2+} as cations, and 53.950% Cl^-, and 44.247% SO_4^{2-} as anions). The 3rd category characterized by presence of the main components with increasing the source of iron elements as a direct effects of Its source (53.514% Na^+, 36.133% Ca^{2+}, 2.736% Mg^{2+} and 6.893 Fe^{2+} as cations, and 24.104% Cl^- and 74.489% SO_4^{2-} as anions). Finally, the 4th category characterized by creating other sources of salts such as nitrates where they equal (28.712% Na^+, 55.486% Ca^{2+}, 1.653% Mg^{2+}, 11.462% K^+ and 2.687 Fe^{2+} as cations, in addition to 35.924% Cl^-, 58.119% SO_4^{2-}, 4.496% HCO_3^- and 1.460% NO_3^- as anions). Within the same context, it could be argued that the fracturing form affected the samples exposed to salty bath contains dues to the presence of the Fe ion, which lead to the creation of sever deterioration forms. These forms are due to the effect of alternative cycles between hydration and crystallization pressures created by the effects of contact with the oxygen and moisture in the open environment. This cycle leads Fe ions to change into hydrous iron oxide (the density is 7.8) which occupies a much larger volume than the parent Iron (the density is 3). This deference leads to the pressure generated in the confined spaces by this volumetric increase is large enough to the fracturing the stone [22].

Mineralogically, the analysis of chemical and mineralogical data by XRD presented in Table 4 proves that the rock-forming is converted by synergetic reaction processes with salinity water into more soluble salts. These salts are *Sulphates* (Thenardite, Mirabillite, Epsomite, Gypsum and Anhydrite), *Chlorides* (Halite and Sylvite), *Carbonates* (Siderite, Natrite and Thermonatrite syn) and *Nitrates* (Nitratine). All of these species of salts amplified by dissolution and transport process of the newly formed minerals where the durability of stone materials is degraded and voids and hairline cracks develop creating more susceptible surfaces to water absorption. [23].

Sulfates are the most common compounds of the soluble salts [24, 25]. Sodium and magnesium sulfates are the most worst of these salt types affecting stone deterioration depending on the dominated degrees of temperature and humidity. On the one hand, sodium sulfates are the main component of more 90% of efflorescence and are the most efficient factor in rock disintegration that due to the sub-florescence faces beneath stone surfaces [26]. They are considered to be results of the transformation of water-free *Thenardite* (Na_2SO_4) to the hydrated phase *Mirabillite* ($Na_2SO_4 \cdot 10H_2O$), [27 -28 - 29] according to the following reaction:

$$Na_2SO_4 \cdot 10H_2O + Vapor \rightleftharpoons Na_2SO_4 + Vapor$$
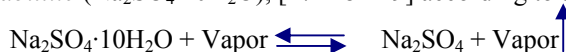
In the present study, sulfate hydration is coupled with volume increase between **70–250%**, as argued before by Price and Brimblecombe [30]. This increase leads to the creation of severe forms of deterioration such as salt crystallization, scaling, crumbling and flaking [31 - 32 - 33 - 34]. On the other hand, the transformation of the water-free *Kieserite* ($MgSO_4 \cdot H_2O$) to the hydrated phase *Epsomite* ($MgSO_4 \cdot 7H_2O$) is associated with volume increase of about **173%** as discussed by Rothert et al. [35]. Both types of salt can form white rims at the surface as efflorescence, at the open ends of the capillaries or just beneath the surface as sub-efflorescence. The crystallization pressure of salts could achieve 200–2000 atmosphere causing volume expansion [36] which can lead to stone crumbling [37], or stone bursting that resulted with hydration action after water absorption [38], depending on several variables especially the dominated rates of air temperature and relative humidity [39]. The presence of *Gypsum* ($CaSO_4 \cdot 2H_2O$) was created through cation exchange reactions between limestone samples and sulfate sources in salinity water path, according to the following reaction:

$$CaCO_3 + Na_2SO_4 + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O + Na_2CO_3$$
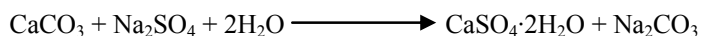
This reaction commonly originates from wet and dry deposition processes in which sulfate products, attack carbonic rocks. The formation of gypsum salty crusts especially both in 1st and 2nd categories is the most important chemical reaction affecting investigated stone
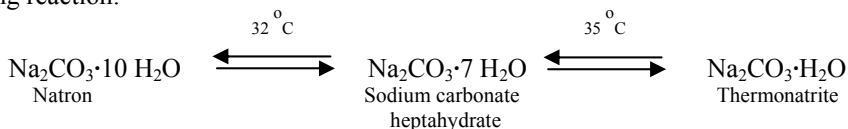
samples causing highly degradation forms as argued before by Wessman [12]. When gypsum is formed on limestone develop thick crusts instead particularly with the presence of catalyst agents such as sources of nitrate as reported previously by Johansson et al. [13]. It is also capable of causing expansion, but is normally linked to loss both of mass and strength [40], in addition to considerable local expansion and cracking especially when formed in large masses. After rising temperature to 42°C *Gypsum* loses water transformed directly into *Anhydrite* ($CaSO_4$) especially in the 2nd category where this process occurs with exacerbation at even at lower temperature with presence *Halite* (NaCl) or *Sylvite* (KCl) [21].

Chlorides, although chloride species are quite common in costal environment, they are very abundant compounds in the Egyptian land. On one hand**,** *Halite* (NaCl) is the main type of salt belonging to these species. Its dissolution is produced with Relative Humidity above 75% for more than 7.5 h, then crystallization-dissolution cycles of the salt can be formed especially with the repetition of these cycles could induce the stone degradation by several types of deterioration forms such as contour scaling and granular disintegration as reported previously by Smith and McGreevy [41]. In our case, halite leads to sever effects on stone samples because of the synergetic reaction between it and soluble sulfate composing both thenardite and hydrochloric acid which lead to the maximum deterioration and corrosion of the stone body especially in 2nd category according to the following reaction:

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

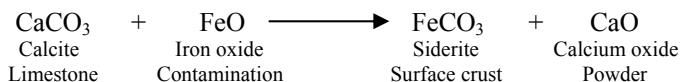Halite   Pollutants   Thenardite
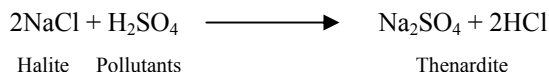
On the other hand, the presence K ion as a potassium source besides Na, Cl, S and Ca lead to the possible presence of minority of *Sylvite* (KCl) characterized by cubic shape crystals because of its ready solubility as argued before by Ganor et al. [42]. In this study the existence of sylvite is due essentially to chemical reaction and ion exchange between Ca as a source of calcite and potassium nitrate as a source of salinity water. It is extremely dangerous because this salt has a high ability to re-crystallize in humid environments [43]. *Bischofite* ($MgCl_2 \cdot 6H_2O$) is a crystalline salt left after water evaporation; it is extremely hygroscopic material and contains insignificant quantities of sulphate minerals. It has equilibrium relative humidity of 33% [44]. Finally, it could be observed that the chloride group is associated with S and Ca (*Gypsum* - $CaSO_4 \cdot 2H_2O$ or *Anhydrite* - $CaSO_4$), as efflorescence observable on halite cubes or forming a homogeneous mixture with halite. This mixture takes rods, round, hexagonal or cubic shapes.

Carbonates are very scarcely mentioned as soluble salts in the deterioration of stone buildings. But in some special cases, they are considered predominant components of many efflorescence particularly in the moisten ground of building materials which characterize the most archaeological sites in Egypt. Experiments have shown that the carbonate salts form three stable hydrated phases with 1, 7 and 10 water moles depending on temperature degree (between 0°C to 30°C) and RH level (50% up to higher to 80%) [20], according to the following reaction:

$$Na_2CO_3 \cdot 10\ H_2O \underset{}{\overset{32\ °C}{\rightleftarrows}} Na_2CO_3 \cdot 7\ H_2O \underset{}{\overset{35\ °C}{\rightleftarrows}} Na_2CO_3 \cdot H_2O$$

Natron   Sodium carbonate   Thermonatrite
                         heptahydrate

In the present study, there are three types of salts belonging to carbonate salts which have the same effects of sulfates [6]. *Natrite* (Na_2CO_3) one of the most important of carbonates known by soda ash or sal soda created through crystallization procedures after evaporated the water [45]. It is a white powder of anhydrous sodium carbonate, which cakes and aggregates on exposure to air due to the formation of hydrates and vice versa by drying and wetting cycles. This leads to the creation of some aggressive and manifold deterioration mechanisms such as migration of the dissolved salts into the stones, internal crystals with disruptive pressure

extracted by crystals for their growth, hydration or thermal expansion, surface efflorescence, creation of habitat favorable for microbiological colonization as reported previously by Camuffo et al. [46]. *Thermonatrite* ($Na_2CO_3 \cdot H_2O$) is thin white layers of salt efflorescence mostly mixed with sulphates [47]. It is a water-soluble mineral form as a surface deposit and it is primarily found after evaporation [48]. Its crystallization in the pore spaces of building stones can produce significant deterioration mechanisms, particularly the expansion mechanisms attributed to hydration pressure (about 70% by volume) during the transition from the water-free phase to the hydrate phase. These mechanisms lead finally to significant deterioration forms [49], such as cracking and fracturing [50]. *Siderite* ($FeCO_3$) mostly resulted from ion exchange in ground water characterized the most of Egyptian soil, where, the substitution of Ca for Fe is limited and due to large difference in size of both ions as explained before by El-Gohary [51] according to the next formula:

$$CaCO_3 \quad + \quad FeO \quad \longrightarrow \quad FeCO_3 \quad + \quad CaO$$

Calcite	Iron oxide	Siderite	Calcium oxide
Limestone	Contamination	Surface crust	Powder

All of these carbonate salts have a volume change of up to and around 300% during hydration caused by changes in temperature and/or humidity–hydration and dehydration, then generated greater pressure [52].

Nitrates have become of significant importance in the decay of historical building materials due to changes in the environment [53]. They are mostly found in cultivated environments and in the environments of decomposing organic matters. The resulted XRD data proved that the most of these salts which affecting the stone samples are *Nitratine* or *Soda Niter* ($NaNO_3$). It is a soluble salt [54], which normally gives rise to thick efflorescence easy to eliminate and of which the disintegrating actions are inferior to those of the sulphates [55]. It is found as efflorescence in hot and very dry environments and very soluble in water such as that it is deliquescent and will absorb water out of the air and turn into a puddle of sodium nitrate solution when exposed to humid air. This salt my have been introduced from external sources such as rising damp from the soil or through some species of microorganisms resulted from the effects of some biological activities [56]. Also, it may be resulted from the bio-deterioration process originating from abundance guano deposits [57] that characterize the most of Egyptian land. This salt leads to a significant deterioration between 10–100 times more gypsum, [58]. Finally, the previous species of salts are strongly connected with water migration and evaporation cycles in walls and lead to several deterioration forms.

Conclusions

The experiments in the present study clearly indicate that saline water is one of the most aggressive factors of deterioration of archaeological limestone. Chemical mechanisms lead to several deterioration forms related to drying conditions. These forms are granular disintegration, alveolar weathering, frequent flaking, multiple-flaking, fissures, mechanical stress, internal strains and disappearance of stone, mortars or plasters superficial zones. Moreover, some other chemical damages and forms especially those related to saturation conditions, such as split off thin overlying layers and formation of grooves, resulted from water accumulation. All of these deterioration forms are followed by different physical and mechanical forms which will be a topic for further research.

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