PHYSICAL DETERIORATION OF EGYPTIAN LIMESTONE AFFECTED BY SALINE WATER

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Abstract

This study is the second in a series of experiments that describe the chemical, physical and thermal properties of archaeological limestone affected by salt and saline water in Egypt. This research aims to study the aggressive physical effects of different types of salts dominated in saline water and their different mechanisms on the acceleration of weathering processes that affect Egyptian limestone. It presents a multidisciplinary approach to characterize, at both micro/macro scales, the behavior of a limestone widely used as a construction material in most of Egyptian monuments when interacting with some types of salt solutions of various concentrations. A systematic optical, morphological, physical and mechanical analysis of the fresh and weathered stone samples were used to evaluate different characteristics through using scientific some techniques such as optical microscope (OP) and scanning electron microscope (SEM). In addition to the using of some special computer programs that were used to define different physical and mechanical properties such as weight changes, bulk density, total porosity, water uptake, water content, thermal dilatation and abrasion resistant. The results proved that all investigated samples were gradually affected by the types of salinity paths and salt concentrations. These results will serve as a database for the future comparison of long term behavior of stones before and after the planned conservation of the entire area. So, it is pertinent to device some scientific methods and interventions to reduce all factors of salt effects and removing their harmful aspects from historic fabric of the archaeological buildings through some scientific recommendations.

Keywords: Saline water; Physical properties; Thermal dilatation; Abrasion resistant

Introduction

Weathering is a natural complicated process that results in the adjustment of internal constituents by the action of physical, chemical and biological factors [1]. Based on several researches, it could be noticed that these actions are rarely the result of just one single factor but they are usually a combination of different agents [2-5]. Different effects resulted by salt weathering are considered some of the most deteriorating factors affecting all components of archaeological buildings and depend mainly on the type of salt, stone characteristics and test conditions [6, 7]. They can be controlled and determined by several variables (chemistry of minerals, types of cement materials and climatic conditions) [8, 9], and are mostly regulated by stone physical properties (porosity or shape of the interior surface) [10, 11]. Physical weathering is the breakdown of rock materials by entirely mechanical methods brought about

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by a variety of causes, i.e. water, salt, wind and temperature, which can significantly alter stone structural and its different properties [12, 13]. Physical weathering resulted by the effects of salt and salinity water is one of the most dangerous and extensive mechanisms [14], this type of weathering can cause some aggressive cycles of decay and degradation forms that affect the buildings in a wide range of environments [15, 16].

These cycles greatly limit the durability of porous building materials [17]. They can produce some aggressive stresses and strains within the building materials [18], leading to the development of some cracks types and micro-fussers, in addition to the increasing of voids inside their body, thus, stones lose their cohesion and may occasionally collapse [6]. This type of weathering mostly creates some forms of deterioration such as salt crystallization (efflorescence, sub-efflorescence and crypto-efflorescence) [7], scaling, crumpling, flaking and cracking. All of these forms lead to severe effects on different optical characteristics and physical properties of the affected stone body which could be summarized in the following sections. These symptoms are widespread in most of the archaeological sites in Egypt both in the southern part of Egypt such as Esna, Edfu, Abydos temples, as well as some Pharaohnic tombs. Furthermore, some Islamic archaeological sites in Northern part of Egypt especially in Fatimid and Mamluk Cairo, and the most of the archaeological sites and Delta (Fig. 1).

Fig. 1. Forms of physical deterioration affecting some Egyptian monuments resulted from the effects of salinity water

**Experimental**

24 limestone samples that were used as a model for simulation study were prepared as cubic 3×3×3cm; the first 1mm of the surface was discarded to avoid contamination features. These samples were subjected to alternative cycles of soaking and drying in four different salinity water paths and they were divided into four groups (A-B-C-D) according to the types of these paths [19]. Then, the different optical, morphological, physical, mechanical and thermal properties of these samples were studied by some scientific tools and techniques such as Optical Microscope and Scanning Electron Microscope, in addition to some computer programs. According to Kumar & Ginell [20] and El-Gohary [21], all weathered samples were submitted to Micro-Abrasion Resistance test to evaluate their relative effectiveness against the effects of different erosion mechanisms and were represented by using SketchUp 6-Pro.

**Results**

Different investigation techniques, tools and computer programs that were used to evaluate limestone samples before and after weathering cycles proved that these samples show
different results according to the types of salinity baths; the results of the previous experiments performed on investigated samples were evaluated as follows:

**a. Optical Features**

Laboratory salt resistance tests which were carried out for evaluating and verifying the weathering susceptibility showed serious differences in their visual appearances compared to the standard sample. Also, they proved that all samples were affected with different grades according to the types of salinity baths as follows:

- The samples belonging to category A, were highly affected, collapsed and completely changed to bordered body, also their color changed to black gray (Fig. 2a);
- The samples of category B, were affected where their visual appearance as their color turned into light yellow, in addition to partly loosing some of their cohesive resistance, (Fig. 2b);
- The visual appearance of category C samples was highly changed and affected, where they turned into dark red color, furthermore, they aggressively lost their cohesive resistance, in addition to presence of some cross-linking cracks (Fig. 2c);
- The samples belonging to category D were partly affected where there visual appearance were colored by dark yellow without loosing there cohesive resistance (Fig. 2d).

**Fig. 2.** The visual appearances of affected samples compared with standard sample

**b. Morphological Map by SEM**

Salt crystallization in the specimens has been studied by FEI Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray system of EDAX. The investigations have been carried out mainly by the use of a back scattered electron (BSE) detector. Low magnifications were used to study salt distribution and location, while higher magnifications were used to investigate crystal shapes. The investigated electronic mapping using SEM of cross sections reveals that there are several harmful forms which affected the substrate of the samples' surfaces by some aggressive kinds of salts (halite, gypsum, anhydrite, thenardite and mirabilite). In addition, it could be noticed that there is a mixture of very fine fragments on the samples' surfaces mostly composed of (kieserite, epsomite, sylvite, natrite and thermonatrite). Furthermore, there is a clear border between the original stone surface and superficial layers resulted from the effects of weathering cycles, in addition to dissolution forms affecting the calcite grains (Fig. 3).
c. Physical Properties

According to Anonymous [22] the physico-mechanical tests of stone samples were conducted at the Conservation Laboratory, Sohag University. Important physical properties had been defined to evaluate the increase or decrease of the durability index of our samples, such as weight changes, bulk density, total porosity, water uptake, water content, thermal dilatation and abrasion resistant, all resulted data could be summarized in the following:

Weight change

The selected samples subjected to aging test generally showed signs of decay by means of measuring the weight loss and the durability of each sample, where weight variations point to that all of these samples were affected as follow.

- The samples belonging to category A (exposed to 20% Na₂SO₄) have a higher index of weight lost (about 12.01%) especially in the 1st stage of weathering where they were collapsed completely after this stage.
- The weight of other categories B, C and D increased where it was in category B (exposed to 1:1 20% Na₂SO₄ and 20% NaCl) (6.99% in 1st stage, followed by 9.62% in 2nd stage, finally by 7.97% in 3rd stage). On the other hand, the weight samples of category C (exposed to 1:1:0.5 of 20% Na₂SO₄, 20% NaCl and 10% FeCl₂) increased, where it was (6.04% in 1st stage and 7.90% in 2nd stage), finally, it highly decreased in 3rd stage where equal 2.10%). Within the same context the weight samples of category D (exposed to 1:1:0.5 of 20% Na₂SO₄, 20% NaCl and 10% KNO₃) also increased as follow (7.11% in 1st stage and 6.76% in 2nd stage, finally 10.21% in 3rd stage).
- The weights of all affected samples increased in the 2nd stage of exposure compared to other stages (Fig. 4a).
Density

The investigations showed that the densities of all samples were slowly affected with different grades according to the quality of salinity paths where, in category A it decreased compared to reference sample of 2.11g/cm$^3$ and equal to 2.109g/cm$^3$ recorded after 1$^{st}$ stage of weathering. On the other hand, category B the recorded densities were 2.3g/cm$^3$ after 1$^{st}$ stage of weathering, 2.35g/cm$^3$ after 2$^{nd}$ stage and 2.39g/cm$^3$ after 3$^{rd}$ stage. In category C they were 2.21g/cm$^3$ after 1$^{st}$ stage of weathering, 2.25g/cm$^3$ after 2$^{nd}$ stage and 2.13g/cm$^3$ after 3$^{rd}$ stage. Finally, the recorded densities in category D were 2.27g/cm$^3$ after 1$^{st}$ stage of weathering, 2.26g/cm$^3$ after 2$^{nd}$ stage and 2.33g/cm$^3$ after 3$^{rd}$ stage (Fig. 4b).
Porosity
The porosities of investigated samples show that there is a high increase in the tested samples after weathering cycles compared to non-affected ones where it was 15.30% and became 20.20% after in category A. Moreover, the recorded porosity indexes of category B is 21% after 1st stage of weathering, 9.55% after 2nd stage and 18.11% after 3rd stage. Also, they became higher in category C 35.55% after 1st stage of weathering, 35.95% after 2nd stage and 41.25% after 3rd stage. On the other hand, the records highly decreased in category D 6.40% after 1st stage of weathering, 3.94% after 2nd stage and 6.87% after 3rd stage (Fig. 4c).

Water up take
The water up take of the samples under investigation showed that there are great differences between before and after finishing the weathering cycles. Whereas water up take was 7.26% before, it became 10.83% after in category A, and it was 10.81% after 1st stage of weathering, then, decreased to 3.55% after 2nd stage and finally increased to 7.36% after 3rd stage in category B. Moreover, the recorded data became higher in category C 16.10% after 1st stage of weathering, 16.03% after 2nd stage and 17.92% after 3rd stage. On the other hand the records decreased in category D where they became 2.82% after 1st stage of weathering, 1.74% after 2nd stage and 2.90% after 3rd stage, (Fig. 4d).

Water content
The investigated samples showed that there are noticeable variations in recorded water content indexes before and after weathering cycles whereas water 0.141% before, and became 2.302% after in category A. Within the same context, the recorded data in category B were 1.914% after 1st stage of weathering, 2.633% after 2nd stage and 2.818% after 3rd stage. Furthermore, the recorded data in category C were 1.978% after 1st stage of weathering, 2.733% after 2nd stage and 3.038% after 3rd stage. Finally, the data were 1.916% after 1st stage of weathering, 2.702% after 2nd stage and 2.702% after 3rd stage in category D (Fig. 4e).

Abrasion Resistant
The results of this test proved that all investigated samples were affected with different grades due to the effects of salts on the external surfaces and internal grins of the samples. In addition to the degradation and solubility of the cement materials of the samples, all obtained results are listed in Table 1 and figure 5.

<table>
<thead>
<tr>
<th>Stages</th>
<th>Ref</th>
<th>S.</th>
<th>A</th>
<th>W L %</th>
<th>D I %</th>
<th>B</th>
<th>W L %</th>
<th>D I %</th>
<th>C</th>
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D = destroyed  
W L % = weight lost  
D I % = depth lost

Fig. 5. The morphological surfaces of affected samples after abrasion cycles
**d. Thermal Properties**

The deterioration of stone through salt is attributed to the volumetric expansion of the salt within the pore space of stone, which can be caused by crystallization/re-crystallization; hydration/re-hydration or thermal expansion processes [23, 24]. High sensitivity determination of thermal expansion of solid materials makes possible the investigation of material properties at low temperatures, where expansion coefficients are small. Also, a high sensitivity method permits us to determine thermal expansion properties of low-expansion materials of high technological interest [25]. According to DIN 52450 [26] thermal dilatation coefficient of each sample was measured for five times, then, calculating the average. All of these measures were determined using a Mitutoyo ABSOLUTE Digimatic Indicator model ID-C112B. Firstly, the samples with known length, were heated at 60°C for 8 h., then were immediately axially fixed on the dilatometer, and the initial and final readings, after other 8h, on the dilatometer were recorded.

*Thermal dilatation coefficient* was calculated according the following formula:

\[
\mu = \frac{(D_I - D_F)}{(L \times (T_I - T_F))},
\]

where, \(\mu\) is the thermal dilatation coefficient \([\text{µm} \, (\text{mm}^2\text{C})^{-1}]\), \(D_I\) is the initial reading of the dilatometer (µm), \(D_F\) is the final reading of the dilatometer (µm), \(L\) is the length of the sample (mm), \(T_I\) is the initial temperature (60°C), \(T_F\) is the final room temperature, 21°C [27, 28].

The average results of the investigated samples proved that the *thermal dilatation* of reference samples was \(6.3 \times 10^{-6}(\text{ºC})^{-1}\), where it decreased to \(5.6 \times 10^{-6}(\text{ºC})^{-1}\) in category A. In category B, the recorded measures were consequently \(9.2 \times 10^{-6}(\text{ºC})^{-1}\) after 1st stage, \(15.7 \times 10^{-6}(\text{ºC})^{-1}\) after 2nd stage and \(15.9 \times 10^{-6}(\text{ºC})^{-1}\) after finishing the 3rd stage. On the other hand, this property decreased in category C where they became \(10 \times 10^{-6}(\text{ºC})^{-1}\) after 1st stage, \(11.5 \times 10^{-6}(\text{ºC})^{-1}\) after 2nd stage and \(8.7 \times 10^{-6}(\text{ºC})^{-1}\) after finishing the 3rd stage. Finally, the samples belonging to category D showed minor differences; where they were \(11.9 \times 10^{-6}(\text{ºC})^{-1}\) after 1st stage, \(9.2 \times 10^{-6}(\text{ºC})^{-1}\) after 2nd stage and \(11.1 \times 10^{-6}(\text{ºC})^{-1}\) after finishing the 3rd stage (Fig. 6).

![Thermal Dilatation](http://www.ijcs.uaic.ro)

**Fig. 6.** The variation of TD among the affected and non-affected samples.

**Discussion**

It is well known that the consequence of salt crystallization phenomena that takes place in porous, channels and crakes in and near an exposed surface is one of the most extensive sources of deterioration affecting natural stone buildings, mortars, plasters and concrete [29]. Furthermore, it could be said that the weathered state of natural stones can be described using a great number of different characteristics. Also, the resistance of stone building materials is determined by their different physical and mechanical properties [30]. Therefore, some examinations have been carried out to evaluate the harmful effects of different phases of salt formation affecting the physical properties of archaeological stone. Some of these properties (density, porosity, water up take, water content and thermal dilatation) were performed to study...
the changes of their parameters, the relation among them and the kind and amount of salt formation.

Visually, analysis of figure 2 and 3 reveals that the evaluation of salt formation, salt crystallization and their distribution affecting the investigated samples, essentially depends on several variables as previously reported by Lubelli et al. [31]. These variables are the kind and concentration of soluble salt in the salty baths, the kind of stone itself, and the effects of alternative cycles between hydration and crystallization pressures as essential processes of masonry deterioration [32, 33]. Where salt formation is highly remarkable in the samples belonging to 1st category which characterized by fluffy white crystals appeared when projecting 15-20mm from the surfaces. The samples belonging to 2nd category also had been visually affected by light yellow color salty powder layers that owe to the effect of some natural impurities present both in thenardite and halite. The samples belonging to 3rd category that also affected visually by light red color, essentially owes to the effect of the presence of Fe ion. Finally the samples belonging to 4th category characterized by the presence of light dark brown color. This color which may have been the result of the chemical reaction between the components of salty bath especially Na and K ions, in addition to the effect of equilibrium relative humidity (ERH) or the effects of Salt contaminated masonry as argued previously by Pickering [34], and Hong et al. [35]. Also, it could be seen that there are typical distributions of salt according to the type and the characteristics of the dominated anion. Whereas the sulphates are mainly concentrated in the lower parts of the samples, the other salt types appear in the upper parts [36].

Physically, it could be said that there rare high variations between the degradation grades affected the stone in different categories which are essentially due to the effects of different weathering parameters [37, 38]. These differences vary between negative and positive variations. Regarding the negative variations (reducing the physical properties), data analysis of the investigated samples, (Fig. 4a, b, c, d and e) points out that the salt weathering phenomena caused severe alterations especially with the presence of some types of clay minerals. These minerals such as montmorillonite veins, or may be due to the high mobility of some types of salts such as Na₂SO₄. Also, there are other external parameters especially the effect of marine aerosols [39, 40] which make the stone tends to be softer, characterized by high deterioration index [5], and lead to serious deterioration patterns [41]. Also, these aggressive effects may be attributed to the susceptibility of the investigated samples to the degradation process especially with presence of internal parameters [42]. Moreover, the effects of the alternative cycles between hydration and crystallization mechanisms those finally lead to the fracturing and bursting of stone material [43]. On the other hand, these positive variations (rising the physical properties), may be due to the accumulation of the salt crystals within the stone pores and the frustrating effects of other salt types especially Na₂SO₄ that led finally to the increase of the pressures caused by both hydration and crystallization mechanisms. Again it could be due to the absorption and saturation coefficients, porosity, pore size and pore distribution as argued previously by Cultrone, & Sebastián [32] and Weber & Zinsmeister [44].

Thermally, the results proved that the decreasing average of thermal dilatation coefficient per unit mass of salt is the lowest for the 1st cat., due to the destruction of the samples which resulted from the effects of crystallization/hydration alternative cycles. On the other hand, the results proved that the thermal dilatation increased due to varying extents in salted samples compared to salt-free samples in all other categories. These increases mainly depend on the type and nature of the salt, in addition to the catalyst agent found, where, the increasing value was 115.87% in 2nd category which contains mixtures of (1:1) of 20% Na₂SO₄ and 20% NaCl. Also, it was 59.30% in 3rd category which contains mixtures of (1:1:0.5) of 20% Na₂SO₄, 20% NaCl and 10% FeCl₂. It was 70.00% in the 4th cat., which contains mixtures of (1:1:0.5) of 20% Na₂SO₄, 20% NaCl and 10% KNO₃. Finally, it can be clearly seen that the thermal dilatation coefficients of the samples are higher after they have been artificially salted than for the salt-
free samples. This result can be attributed to the relatively high thermal dilatation coefficient of salt minerals as reported previously by Correns [45]. These increases in the samples depend upon many factors such as, stone types, salt content, porosity, pore size and pore distribution as argued before by Walker et. al. [46], Fang [47], and Kassem et. al. [48], in addition to mineralogical composition and dominated environmental situation [49-52].

Conclusions

The importance of the current research in the conservation field is to know the physical effects caused by the aggressive effects of salt deterioration on monumental buildings and its different component "stones, mortars and plasters". The studied samples in-situ and laboratory tests provide an overview of the present state of the deterioration of several monumental buildings along Egypt, which were the result of the effects of different types of salts. The results proved that all investigated samples were affected gradually according to the types of salinity paths and salt concentrations. These results will serve as a database for the future comparison of long term behavior of stones before and after the planned conservation of the entire area. So, it is pertinent to devise some scientific methods and interventions to reduce all factors of salt effects and removing their harmful aspects from historic fabric of the archaeological buildings through some scientific recommendations which could be concluded as follows:

- scientific diagnosis through using several methods and analytical techniques;
- consequences methods of cleaning and desalination should be used according to deterioration status;
- removing the different salt types through applying suitable techniques;
- protecting stone surfaces against all sources of saline-groundwater and acid rainwater.

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Received: July, 03, 2013
Accepted: November, 15, 2013