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THE IMPACT OF SALT CRYSTALLIZATION ON THE BUILDING STONES OF AL-AZHAR MOSQUE FROM HISTORIC CAIRO – EGYPT

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Abstract
Al-Azhar is one of the oldest mosques in historic Cairo. It was constructed by the Fatimids between 970-972 A.D. Most of historic Cairo buildings included Al-azhar are made mainly of carbonate stones that belong to Eocene Mokattam formation. These carbonate stones exhibit considerable damage related in many cases to the salt crystallization. Mineralogical investigation revealed that the studied samples can be classified as pure limestone to dolomitic limestone. The samples extracted from deteriorated surfaces showed clearly the crystallization of gypsum and halite filling the pores of stone material when they examined by Scanning Electron Microscope (SEM). These observations were confirmed by the means of Ion Chromatography (IC) analysis which in some samples the accumulations of chloride, sulphates and nitrates were high compared with the quarry samples. The strength of sample extracted from a surface where the salts occurred as subflorescence was showing a significant reduction by almost 42% while where salts occurred as efflorescence, the strength of the extracted cores showed slight reduction.

***Keywords**: Stone Decay; Mokattam Limestone; Salt Crystallization; Historic Cairo*

Introduction

Salt crystallization within the pores of the stone material is considered the main reason of deterioration [1-3]. The most common way for the salts to enter into the stone material is by capillary rise from the ground or by Infiltration of rainwater and sea-spray [4-7].

In the majority of Egyptian Limestones, NaCl is naturally occurred [8-11], with low concentration ranged from 5 to 10mg/L [12]. The ground water with its content of salts; chlorides, nitrates and sulfates considered the most important saline supply for the buildings in Egypt [13]. Other sources of salts include salt spray (chlorides), air pollution (sulfates), soil and human activity (nitrates) [14-15].

The rise of the ground water level under the most of the structures at historic Cairo is main problem of this case study. According to certain authors, the extent of damage and salt content in the walls with rising damp are divided vertically into four zones according to [16-18] where the lower zone has high moisture and saline contents followed by the intermediate zones where the damage always happened and finally the upper zone which marking the end of rising moisture that happened due to the deliquescence of salts.

The effect of salts in the building materials is always related to the changes of the environmental condition i.e. temperature and relative humidity [19-22] and the damage mainly

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happened due to the forces that are induced by the crystallization of salts and usually exceed the tensile strength of the average construction materials [7, 23].

The main objective of this research is to study the impact of the salt crystallization on one of the most important structures in historic Cairo by investigating some samples extracted from the building and comparing the obtained results by the ones of fresh samples extracted from Mokattam limestone quarry in Cairo.

Experimental part

Material

Most of the historic Cairo properties are made of Eocene limestone outcrops which located in the boundaries of Cairo [24]. Mokattam limestone plateau in the east of Cairo is main source of quarrying stones that have been used in the construction of most of Islamic stone monuments including Al-azhar mosque [25].

To understand the salt weathering effect on Al-azhar building, ten core samples (~45mm diameter and 50mm length) have been extracted from different facades of Al-azhar (Fig. 1) and meant to represent indoor/outdoor environmental conditions and deteriorated/preserved masonry stone blocks.

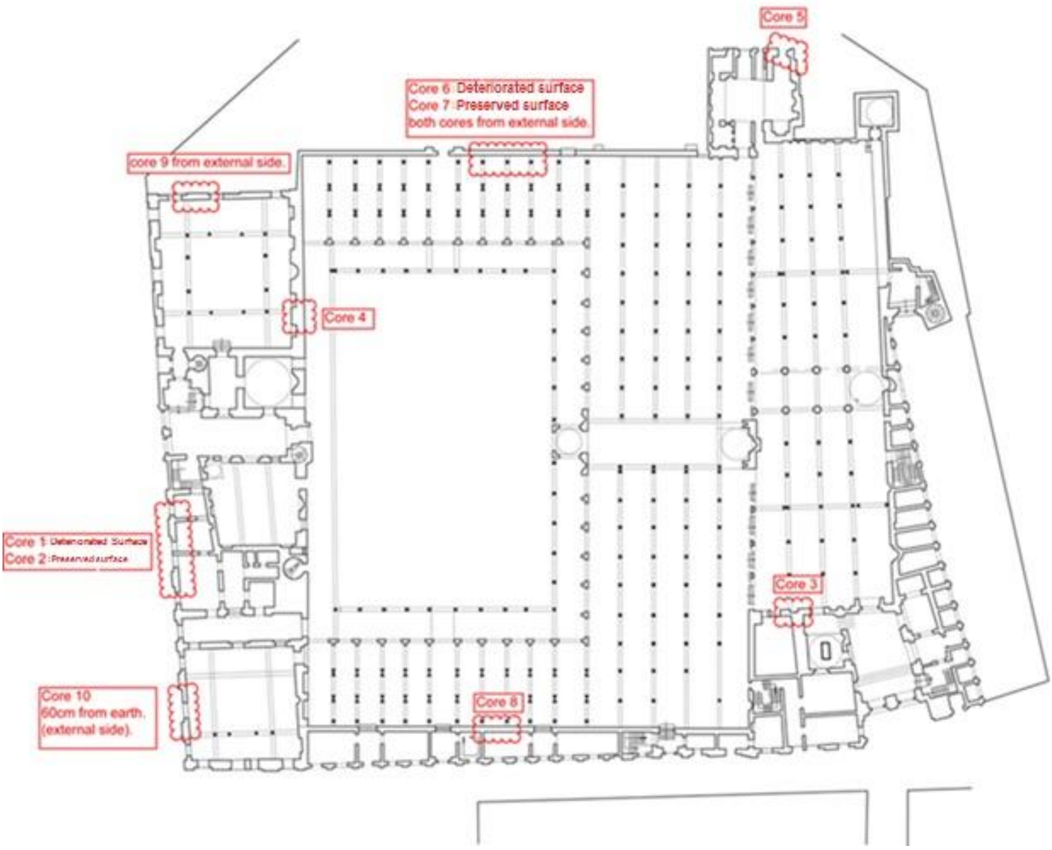

Fig. 1. The plan of the sampling location from the different facades of Al-Azhar

Methods

The petrographic investigation was based on the examination of a thin section from each of the tested samples using polarizing microscope (Leica DM 750P) and images captured using a digital camera. For further specifications of the mineralogical composition X-ray powder diffraction (XRD) by using a classic Philips X'Pert diffractometer (powder method) to determine the mineralogy of all the tested samples. The pattern was run with CuKα radiation (λ = 1.542Å) at 40kV. The scanning was limited from 2θ equals 2º to 60º. The crystallization of the salts within the pores of the studied samples were investigated with Scanning Electron Microscopy (SEM - Philips XL 30) attached with an Energy Dispersive X-ray (EDX) unit. Samples have been shaped in the form of a cube with 1cm side and were coated by gold.

Porosity is the most important physical property of rocks for the study of buildings and monument stones decay because it determines the accessibility of water and saline into the stone material therefore it gives an indication of the susceptibility of the stone to deterioration.

The porosity of the tested samples was measured as:

$$\varphi = V_V/V_T, \quad (1)$$

where: V_v - is the volume of the void space and V_T - is the bulk volume of the sample.

Stone density of the tested specimens was very important parameter to be measured. Generally, a stone with higher-density is probably harder, less porous, and stronger [26]. The tested samples were weighed and density was determined as:

$$\rho = m/V, \quad (2)$$

where: m - is the mass of the specimen and V - is its bulk volume (EN 1936).

The absorption of the water into the rock may affect its durability under salt crystallization conditions. The water absorption is the maximum water absorption capacity showed by the stone sample. The absorption of water is affected by the pore system of the stone and the pore connectivity [26-28]. The water absorption of the investigated samples was measured by using ASTM D6437 – 10 where:

$$\text{Water content (\%)} = [(\text{saturated mass - dry mass})/\text{dry mass}] \times 100 \quad (3)$$

Ion Chromatography (IC) (compact IC 761 Metrohm) was used to compare the salt content of the studied samples and the quarry sample. The anions of interest (Cl^-, SO_4^{2-} and NO_3^-) have been separated and measured.

In this study the strength of studied samples was assigned by measuring both Uniaxial Compressive Strength (UCS) and Tensile strength. The compressive strength was performed by using a hydraulic pressing machine equipped with REP transducers type TS 5t, combined with two strain gauge transducers REP TLDT 5mm. The tensile strength measurements were determined by the means of the "Brazilian test" and according to technical specifications by ASTM D3967 device.

Results and discussion

Visual observations

The observation of the indoor and outdoor facades of Al-Azhar showed that the building is suffered from the salt crystallization as subflorescence which caused a clear scaling of the stone surfaces in some blocks (Fig. 2). The North-West outdoor facade of the building exhibited loss of the surface material in the same level and the crumbling of some stone blocks (Fig. 3). Salts in the North-East indoor wall with rising damp are represented in figure 4 where a notable flaking is developed in the upper zone.

Fig. 2. The development of salt crystallization observed in the eastern outdoor facade with scaling of the outer surface

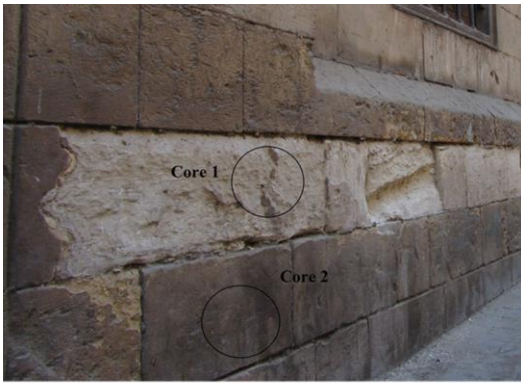

Fig. 3. Damage patterns (loss of surface and crumbling) which noticed in the north-west outdoor facade

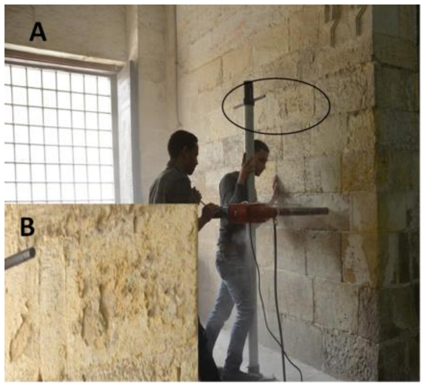

Fig. 4. **A** - general view of indoor facade with rising damp and **B** - close view of the marked area showing flaking of limestone surface

Petrographic investigations

Optical microscopy investigation revealed that all of the studied samples are carbonate rocks with abundant of calcareous micritic interclasts and some dispersed bioclasts (Mollusca shells) and detrital quartz crystals were noticed in sample C6 (Fig. 5).

Dolomitization is the main diagenetic processes showed by the studied samples. It represented mainly by the partial replacement of the original calcitic material and confirmed by the development of medium grained rhombs clasts of dolomite (Fig. 5 - C2) and well-developed euhedral dolomitic crystals (Fig. 5 - C9). The partial dissolution of the dolomitic crystals, leaving behind some relatively hollow crystals can be noticed in C2 (Fig. 5).

A plaster sample (labeled C8) was examined and is characterized by the presence of calcareous and siliceous aggregates surrounded by fine-grained lime matrix (Fig. 5). The plaster sample (Fig. 5 - C8) is lime mortar with quartz aggregates and calcareous lumps.

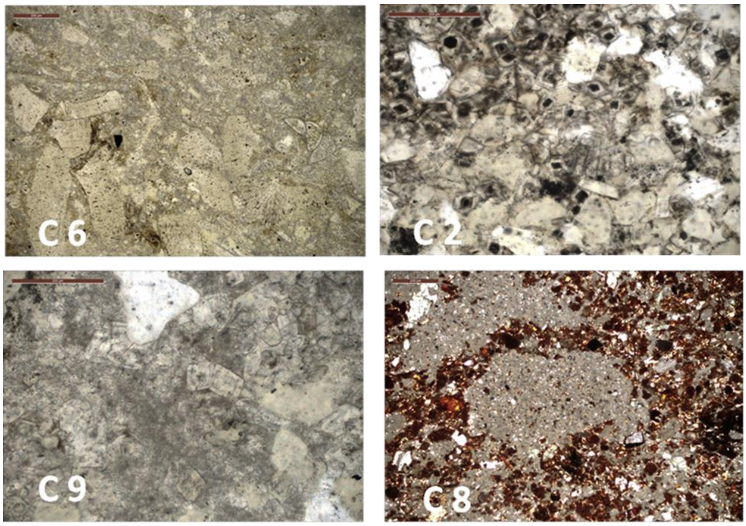

Fig. 5. Thin section photomicrographs of the studied stone samples. Scale bar on all images is 200μm and photos taken under plane light except of C8 in crossed polarized light

Table 1. The XRD analysis data of the tested samples and a descripition of the extracted surfaces

Tested samples	Surface/Environment	Mineral composition			
		Calcite $CaCO_3$	Dolomite $CaMg(CO_3)_2$	Quartz SiO_2	Gypsum $CaSO_4 \cdot 2H_2O$
Core 1	Deteriorated/outdoor	85	-	15	-
Core 2	Preserved/outdoor	16	84	-	-
Core 3	Efflorescence/indoor	47	48	5	-
Core 4	Efflorescence and cracks /indoor	76	-	13	11
Core 5	Deteriorated/indoor	92	-	8	-
Core 6	Subflorescence/outdoor	85	-	7	8
Core 7	Deteriorated/outdoor	69	27	4	-
Core 8	Plastered/indoor	34	11	19	36
Core 9	Preserved/outdoor	43	55	2	-
Core 10	Deteriorated/outdoor	88	2	10	-

The investigation of the studied cores by SEM revealed that all the samples extracted from deteriorated surface contained salt crystals crystallized within the pores of the stone material. The most dominated salts are gypsum and halite. Salts are mostly. Gypsum showed different morphologies including acicular crystals (Fig. 6 - C4, C5) and elongated fibrous crystals (Fig. 6 - C1-a). The development of euhedral to subhedral cubic crystals of halite is clearly seen in C6-a, C6-b and C7 (Fig. 6). The growth salt within the pores leads to the initiation of some micro-crakes formation (Fig. 6 - C1-b, C6-b). The disintegration of stone matrix (Fig.6 - C10) may be also related to the existence of the salts.

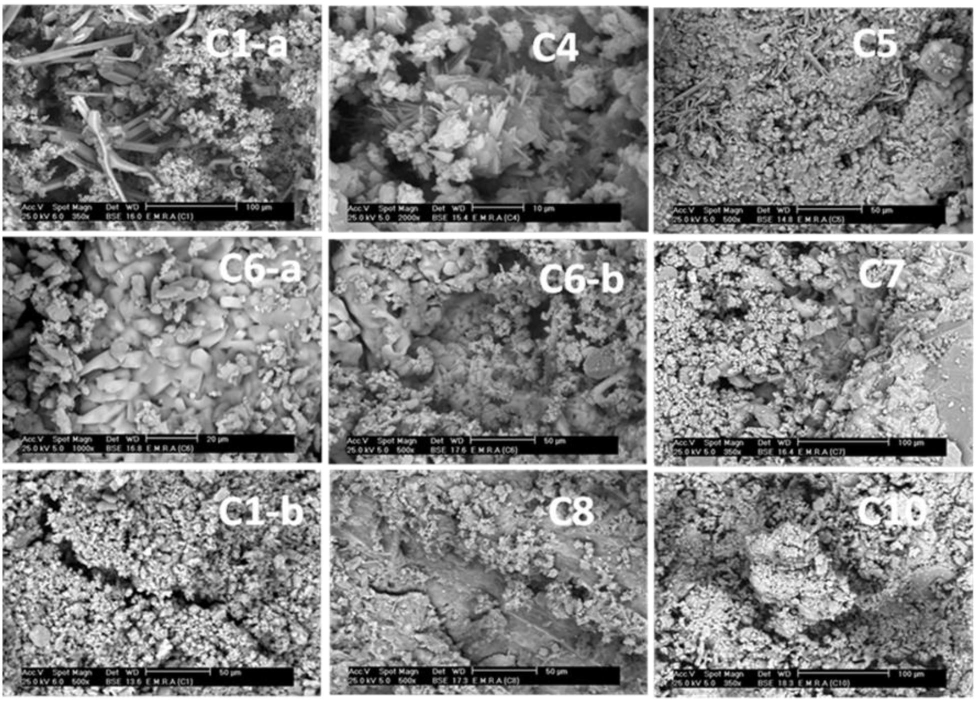

Fig. 6. SEM images showed needle shape crystals of gypsum (C1-a, C4 and C5) and halite crystals (C6-a, C6-b and C7). Crystals growing within the stone pores causing micro-crakes (C1-b and C8) and disintegration of the micrite (C10)

Physical properties

The samples have been extracted from deteriorated surfaces show noticeable increase in the porosity ratio, for example the porosity ratio of Core 1 and Core 10 equals to 20 and respectively 21% while their bulk density show slight decrease compared with the rest of the samples and this is might be explained due to the filling of the pores due to salt growth (Table 2). The minimum value of the porosity ratio showed by C3 sample which extracted from surface showed the crystallization of salts as efflorescence leaving empty pores behind. The water absorption ratio as expected increased in the cores that have more pores (C1 and C10).

Table 2. The physical properties of the studied core samples

Tested samples	Physical properties Water absorption wt.%	Porosity vol. %	Bulk density g/cm^3
Core 1	10	20	2.03
Core 2	9	18	2.00
Core 3	5	10	2.20
Core 4	8	18	2.13
Core 5	8	16	2.13
Core 6	9	19	2.10
Core 7	9	17	2.00
Core 8	8	16	2.00
Core 9	10	21	2.10
Core 10	88	2	10.00

Salt content

Figure 7 shows the results of the ion chromatography analysis of different samples where Cl^-, SO_4^{2-} and NO_3^- concentrations varied in relation to the state of the extracted surface. Most of the samples that showed high salt concentrations are exhibited some degree of deterioration. In addition, the samples that illustrated clear precipitation of gypsum crystals in SEM images (i.e. C4 and C5) have high ratio of SO_4^{2-}. The high accumulation of Cl^- (51.5mg/L) was found in Core 6, which has been extracted from a surface with obvious subflorescence and as well in the SEM images. This sample showed halite crystallization within the pores with taking in consideration that this sample has also high amount of SO_4^{2-} (46mg/L). The disintegration of the samples was also related to their content of salts, as in sample C10 where it has high NO_3^- (22mg/L) and Cl^- (33mg/L) contents. Most of the samples extracted from outdoor facades showed high concentrations of salt ions.

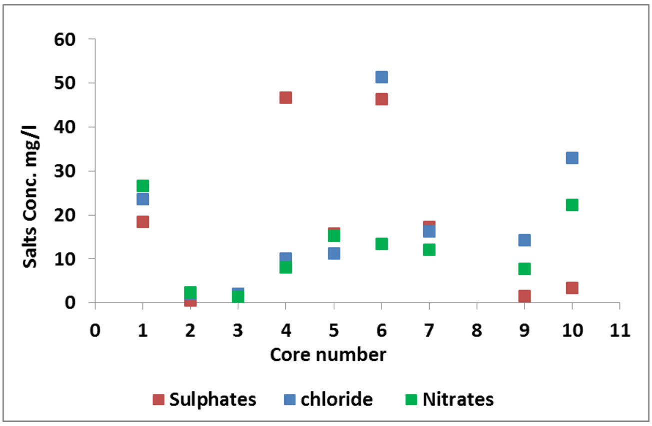

Fig. 7. The concentrations of different ions on the studied samples

Mechanical Properties

Table 3 showed stone strength results of the studied samples. A clear correlation between strength values and the salt ions concentrations can be noticed. Core sample 10 exhibited the less compressive (10MPa) and tensile (2MPa) strengths, has the highest concentration of both Cl^- and SO_4^{2-} (51.5 and 46mg/L respectively) and it was extracted from a surface displaying subflorescence salt crystallization mode. Also, most of the samples exposed to outdoor conditions (C1, C7, C10) have less strength values which highlights the importance of the environmental conditions effect on controlling the rate of weathering and the evolved subsequent decay [20, 29-33].

Table 3. Compressive and tensile strength measurements of the investigated samples

Tested samples	UCS (MPa)	Tensile Strength (MPa)
Core 1	13.7	1.8
Core 2	15.0	2.5
Core 3	15.3	4.3
Core 4	15.2	4.3
Core 5	15.3	1.6
Core 6	10.0	2.0
Core 7	12.6	2.1
Core 9	12.8	2.6
Core 10	13.0	2.4

Conclusions

In this study, the investigations of Al-Azhar building stones have been conducted through assigning the petrographic, physical and mechanical properties and salt ion concentrations measurements. From the obtained results, an evident correlation between salt content and the arising deterioration patterns in the different facades can be obviously noticed. In addition, the relation of the compressive and tensile strengths of the investigated cores and their salt ions concentrations is very distinct. The results showed that the higher the salt ions concentration the lesser the stone strength. The results also showed that the outdoor environmental condition promoting more the deterioration of the stone material and therefore the loss of the stone strength. Thus, the case study presented in this paper can be considered as a further confirmation that pre investigation of historic building stones is a valuable to the decision-making for the restoration and structural consolidation projects.

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