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Role of Investigations and Analytical Methods in Study of Archaeological Stone Ornaments's Deterioration and its Treatment

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Summary. Treatment and conservation of archaeological stone ornaments depend on studying phenomena and factors of their deterioration by various investigations and analyses. Stone ornaments and mortar samples were collected from Azbak AL-Yusufi Madrasa that was built in (1495 A.D./900 A.H) from Mamluk period. Examination and study of these samples have been carried out using scanning electron microscope (SEM), polarizing microscope (PLM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). It was found that crystallization of halite salt in presence of under ground water was the important factor in deterioration of stone ornaments. Laboratory experimental study was carried out using some selected isolating and consolidating materials that have been applied on the models. Estel 1000 was the best consolidant and Nitocote SN 502 was the best isolating material.

Introduction

Archaeological buildings in Egypt include many limestone ornaments that commonly have been used in decoration of walls and facades. There have been worked by engraving techniques. Azbak AL-Yusufi Madrasa that was built in Cairo in (1495 A.D./900 A.H.) from mamluk period includes limestone ornaments.(1) In Cairo, like elsewhere in industrial cities, thousands of tons of Sulphur dioxide annually released by all sorts of fuel and car exhausts have been the main cause of the limestone type monuments decay.(2) The basic chemical reaction is that of sulphur dioxide, which when combines with atmospheric oxygen and moisture, produces, sulphuric acid.(3) This acid reacts with limestone that is composed, essentially, of calcium carbonate producing hydrated calcium sulphate as a salt. On the other hand, sewage water and under ground water contain different salts specially chlorides, sulphates and nitrates. These soluble salts migrate through the building materials from the soil by capillary system to a considerable height in the walls of Archaeological buildings which include stone ornaments because of evaporation, soluble salts deposit on or beneath the stone ornaments and crystallize in different phases causing various types of deterioration phenomena.[4] In addition, the chemical composition and structure of the stone, the location on a building, the impact of the bacteria, soot, subsurface water soluble salts migration[2] must be considered as shown in Fig (1). Investigations and Analytical methods such as, polarizing microscope (PLM), scanning electron microscope (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) can determine factors of the deterioration phenomena. Deteriorated ornaments need to consolidate and isolate their surfaces using consolidates and water repellent polymeric products in order to improve the mechanical properties or to prevent solutions through penetrating the pores. The consolidating action of the polymeric products occurs according to the adhesive action, which the inorganic molecule is able to establish with the various detached stone grains.[5] The water repellent action is carried out by the organic part. Some products may carry out a water repellent action, due to the presence of alkylic groups, as well as a consolidating action, due to the presence of -Si-O-bonds, which, as a consequence of hydrolysis, from -Si-O-H groups, responsible for the hydrogen bond which occurs with the material accessible surface.[6]

Fig. (1) Photos of Azbak limestone ornaments showing erosion, efflorescence of salts, discoloration, chipping and disintegration between grains.

Experimental

Materials and Methods

Analytical study have been carried to selected stone and mortar samples which were taken from stone ornaments of Azbak AL-Yusufi Madrasa by Polarizing Microscope [PLM], Scanning Electron Microscope [SEM] X-ray diffraction (XRD) and Energy dispersive X-ray analysis [EDX]. Four consolidating materials have been examined to consolidate the stone ornaments namely; Estel 1000 (Ethyl Silicate, 3% in white spirit), Paraloid-B82 (Methyl Methacrylate 3% in aceton), Nitocote SN 502 (Silane/ Sioxane Solution in organic solvent ready to use) and Wacker 1311 (Silane/Siloxane micro emulsion 9% in water). The consolidating materials have been applied on stone samples from Azbak AL-Yusufi Madrasa. The bases of their evaluation are measuring their penetration depth within the stone, examining surface changes after using each resin, determine the changes in the physical and mechanical properties(7) and examining stone durability after consolidation and exposing samples to artificial aging to find out which resin verify highest stone strength to weathering processes.(8)

Artificial Weathering

The following experimental conditions used for the purpose of artificial weathering aiming to simulate and determine as well as possible of the actual cause of environmental deterioration to quantify the durability of the treatments.(9)

1- **Wet-dry cycles**: the test consisted of successive immersion and drying 40 cycles were carried out as follows: 14h total immersion in distilled water then 8 hours in an oven at 60^{o}c.

2- **Salt crystallization weathering**: the samples were subjected to cycles as follows: 6 hours of total immersion in a saturated solution of sodium sulphate then 24 hours of exposure to air in normal room conditions then 16 hours in an oven at 60^{o}c.

3- **Acid water weathering**: 30 cycles using H_2SO_4 (3%) then 20 cycles using H_2SO_4 (5%) were carried out.(10) All tests were applied on stone samples measuring 5x5x5cm (3 samples per treatment, compared against 3 untreated samples).

Results and Discussion

Polarizing Microscope (PLM)

Two types of limestone samples were examined and, it was found that: the yellow limestone under PLM consists mainly of fine-grained calcite crystals besides presence of iron oxides, quartz, clay minerals and fossils fig (2) while, the white limestone includes nummulite fossils in a fine-grained matrix (biomicrite) besides presence of clay minerals, a little a mount of iron oxides and some grains of quartz Fig (3) these components increase the rate of stone decay.[11]

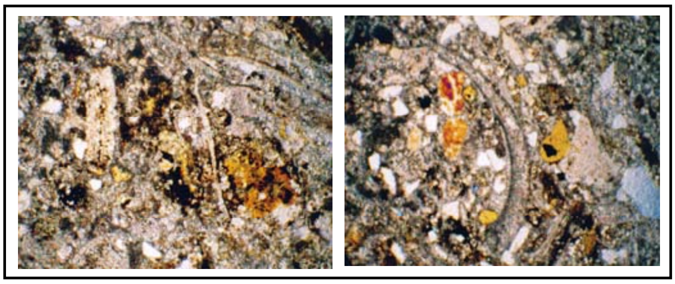

Fig. (2) Thin section photomicrographs showing iron oxides, clay minerals, fossil and grains of quartz in a mass ground of fine-grained calcite. 4X (C.N).

Fig. (3) Thin section photomicrographs showing equatorial section of nummulites Sp., clay minerals in a fine- grained matrix (biomicrite). 10X (C.N).

Scanning Electron Microscope [SEM]

When the limestone samples were examined by [SEM], disintegration between calcite crystals and the stone lost the binding materials between grains by the effect of salts crystallization were found,[12] Fig. (4).

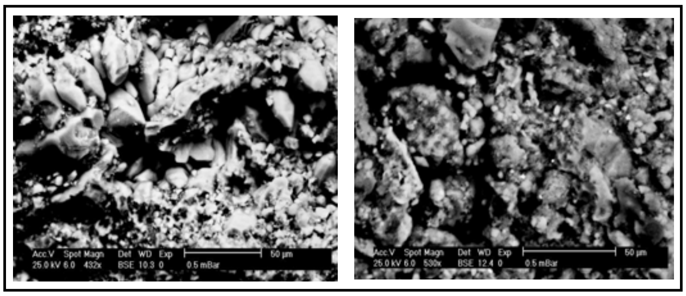

Fig. (4) SEM photomicrographs showing the collaps of internal structure and salts crystallization between grains of limestone ornaments.

X-Ray Diffraction analysis [XRD]

XRD data shows that, the yellow limestone consists of calcite $CaCO_3$, Card No. (5-0586) in addition to dolomite $Ca,Mg(CO_3)_2$, Card No. (11-078), and halite, NaCl Card No. (5-0628) Fig. (5-a). The white limestone consists mainly of calcite in addition to quartz SiO_2 Card No. (5-0490) Fig. (5-b). The mortar consists of calcite, dolomite, quartz in addition to halite; gypsum Card No. (6-0046) and anhydrite, Card No (6-0226) Fig. (5-c). When the water evaporates from soluble salts as chlorides, it leaves behind concentrations of salt solutions which crystallize on the stone surfaces and between mineral grains of stone, this process cause disintegration and deterioration of stone.(13)

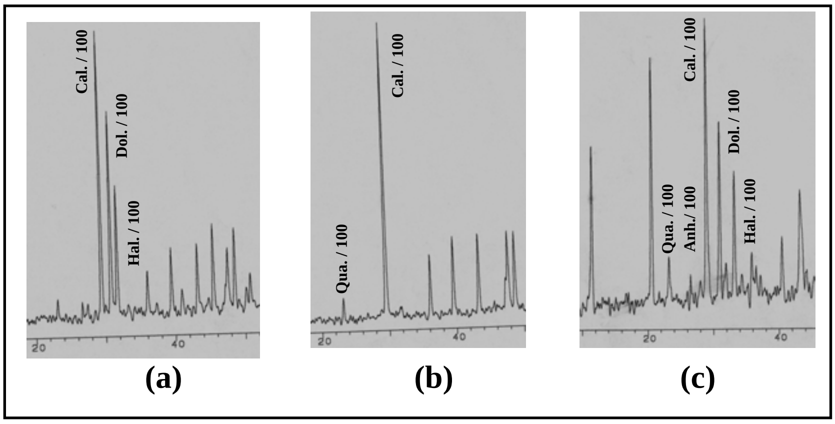

Fig (5) shows XRD patterns of
a: yellow limestone,
b: white limestone,
c: mortar

Energy dispersive X-ray analysis (EDX)

EDX data shows high content of calcium related to calcite mineral, silicon and aluminum due to clay minerals, silicon due to quartz mineral, iron related to iron oxides, sodium and chlorine due to presence of halite salt fig (6).(14)

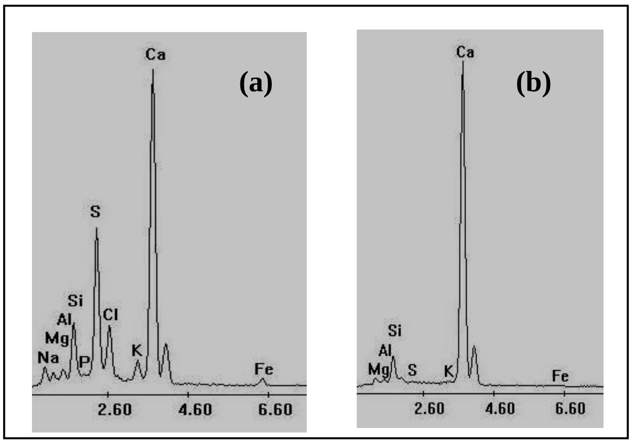

Fig. (6) shows EDX patterns of limestone ornaments of Azbak Al Yusufi Madrasa .
a: yellow limestone.
b: white limestone .

Treatment and conservation processes

Stone samples which have been treated with polymeric products and exposure to artificial weathering show that Estel 1000 (maximum increasing of compressive and tensile strength) given the best result in consolidation and Nitocate SN 502 (maximum reducing of porosity and water absorption) given the best result in Isolation of stone surfaces, total results seen in table No. (1) Estel 1000 and Nitocote SN 502 don't change stone surface color, examination by SEM shows good penetration and good coating of stone, Fig. (7).

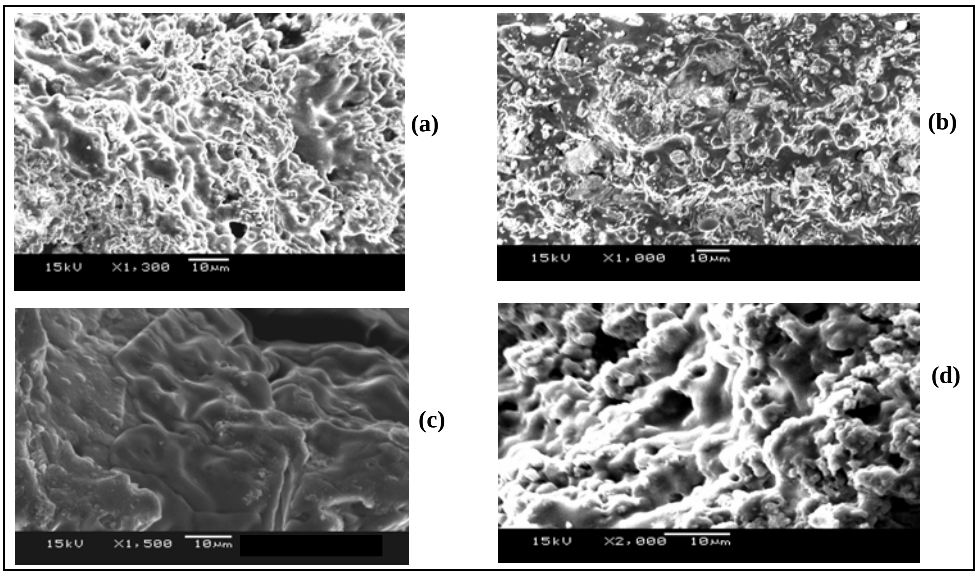

Fig (7) SEM photomicrographs after treatment
a: the forming of resin Estel 1000 with best penetration depth.
b: the forming of resin Nitocote SN 502 with best coating.
c: thick layer of paraloid –B82.
d- the forming of resin wacker 1311.

Table (1) The physical and mechanical properties of limestone samples before, after treatment and artificial weathering

Property	Estel 1000			Paraloid–B82		Nitocote SN 502		Wacker 1311	
	Before	After	Changes %	After	Changes %	After	Changes %	After	Changes %
Bulk Density gr/cm^3	2.2	2.6	18	2.3	4.5	2.4	9	2.3	4.5
Water Absorption%	7.3	2.3	69	4.2	43	0.4	95	1.8	75
Porosity %	14.6	3.6	75	4.9	66	0.9	94	2.1	86
Comprasive Strength Kgm/cm^2	175.6	263.8	50	239.6	36	232.7	33	223.9	28
Tensile Strength Kgm/cm^2	24.3	36.6	51	31.8	31	29.2	20	26.3	8

Conclusion

Deterioration, erosion and disintegration of stone ornaments occur by air pollution, moisture and soluble salts migration. The investigations and analysis of samples showed that the crystalline chlorides exert a pressure on the pores that cause disintegration and cracking of stone and change it into a brittle mass. The stone contains clay minerals and iron oxides that increased deterioration of stone. The experimental study showed that Estel 1000 was the best consolidant of the stone ornaments of Azbak AL-Yusufi Madrasa and Nitocote SN 502 was the best isolating material.

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