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Analysis and Preservation of Marble in Archaeological Buildings

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Summary. The weathering of marble in archaeological buildings depends on its chemical and morphological properties in addition to external factors such as, climatic conditions, amount of air pollutants, under ground water and salts crystallization. Prince Saraghatmash Madrasa is one of the Islamic archaeological buildings in Cairo, that was built in (1356 A.D./757 A.H.) from Mamluk period[(1)]. It includes deteriorated marble objects. Marble samples from these objects were taken. X-Ray diffraction (XRD) was carried out for marble samples. Binocular Microscope, Polarizing Microscope (PLM) and Scanning Electron Microscope (SEM) were used. Physical and mechanical Properties of marble were determined. Rhodorsil RC90 was the best polymeric product in consolidation and isolation according to laboratory experimental study. Treatment and conservation of five marble objects from Prince Saraghatmash Madrasa were carried out.

Introduction

Marble is an important stone in archaeological buildings especially Islamic architecture. It has been used in different purposes for example, floors, fountains, slabs, dados and mosaics. The compactness of the marble makes its relatively resistant to deterioration. Its weak point is the heterogeneous crystals in grain sizes, coupled with the completely random alignment of the crystals that so called mosaic texture.[(2)] The differential thermal expansion with the single calcite crystals. (Contemporary elongation and contraction along orthogonal directions) and the different alignment of adjacent crystals causes the surface particles to break a part when subjected to temperature changes. This effect is compounded by the cleavage of the calcite crystals.[(3)] Deterioration phenomena of marble in archaeological buildings include scaling, exfoliation, powdering, fissuring, discoloration, salt efflorescence, biological patinas and black incrustation.[(4)] These deterioration phenomena occur because of various factors for example, salts crystallization, air pollution, microorganisms and moisture.[(5)] Marble objects of Prince Saraghatmash Madrasa have been suffered from presence of dusty black layers, cracks, and erosion, missing parts, exfoliation and iron stains. Fig. (1, a-b)

Experimental

Materials and Methods

Marble samples have been taken from prince Saraghatmash Madrasa objects and studied by Binocular Microscope, Polarizing Microscope [PLM], Scanning Electron Microscope [SEM] and X-ray diffraction analysis [XRD].

Fig (1) a: Photos of marble objects from Prince Saraghatmash Madrasa shows dirt layer, gypsun patches and black incrustation.

Fig (1) b: Photos of marble objects from Prince Saraghatmash Madrasa shows missing part and disintegration of three tops in the marble cenotaph and a decorated marble plate

Experimental study has been carried out to select the best polymeric product in consolidation and isolation of marble objects. Three consolidant materials(6) have been examined as follows:

1- **Wacker 290** (Alkyl–Alkoxy Siloxane) 5% in white spirit.

2- **Rohdorsil RC 90** (Tetra Ethoxy Silane+Methyl Phenyl Poly Siloxane) 5% in white spirit.

3- **Motema 30** (Poly Ethyl Silicate) 5% in Ethanol+**Paraliod–B72** 3% in Aceton and Toluene (1:1) [Mixture 50/50].

Evolution of consolidation materials based on determinative the changes in Physical and mechanical properties after treatment and exposure samples to artificial aging and examination color surface changes to choose the best consolidant.(7)

Artificial Weathering

Artificial weathering have been carried out as follows:

1- **Wet-Dry Cycles**: 40 cycles (18 hours total immersion in distilled water then 6 hours in an oven at 60ºc)

2- **Salt crystallization**: in a saturated solution of sodium Sulphate then 16 hours of exposure to air in normal room conditions then 18 hours in an oven at 60ºc.

3- **Acid water weathering**: 30 cycles have been carried out using H_2SO_4 (5%) all tests were applied on marble samples measuring 3x3x3 cm (3 samples for each treatment)(8).

Results and Discussion

Binocular Microscope Examination

Examination shows that very inequigranular grains of calcite, saccharoidal texture of marble and black, reddish, fine, atmospheric particles and grains of quartz, fig (2). In addition to yellowish-grey, translucent crust. It is a mosaic texture, almost devoid of porosity.

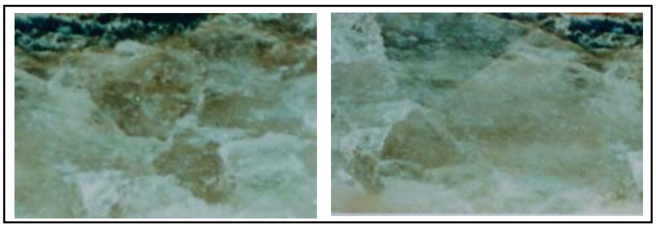


Fig (2) Polished sections of marble objects show very inequigranular grains of calcite and black crust.

Polarizing Microscope (PLM) Examination

Under polarizing microscope the thin section of fragments taken from marble objects shows that the major mineral is calcite. The calcite crystals have irregular faces and highly variable grain size, approximately, from less 0.1mm to 0.8mm, the cleavage planes of the calcite crystals and the presence of rare and very little amount of opaque minerals, the dimensional variability of the calcite crystals and their random orientation (absence of preferential alignments) fig (3).

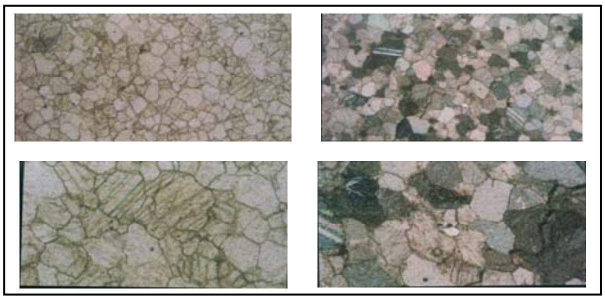


Fig (3) shows that it is a mosaic texture, the calcite crystals have irregular faces and cleavage planes.

Scanning Electron Microscope [SEM] Examination

Examination by [SEM] shows that, erosion of calcite crystals, presence of salts because of chemical reaction with climatic conditions, voids and disintegration between grains by crystallization of salts stresses and lost of binding material[9] fig (4).

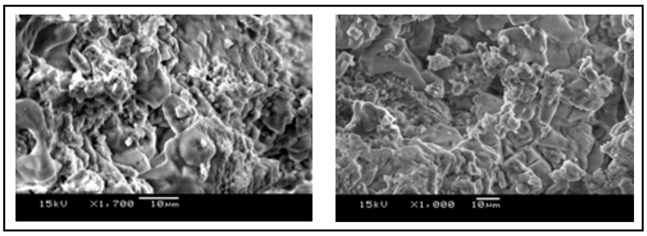


Fig (4)
Shows voids due to lose of binding material and salts crystallization between

X-Ray Diffraction Analysis

XRD data shows that, the examined sample consists of calcite $CaCO_3$, Card No. (5-0586) in addition to gypsum $CaSO_4.2H_2O$ Card No. (6-0046), quartz SiO_2, Card No. (5-0490), halite Card No. (5-0628) and dolomite Card No. (11-078). The surface of the marble is covered by a crust of hydrated calcium sulphate related to reaction with air pollution in presence of moisture[10] fig (5).

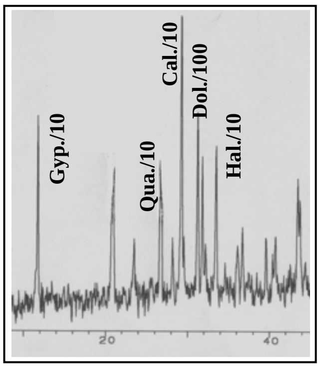
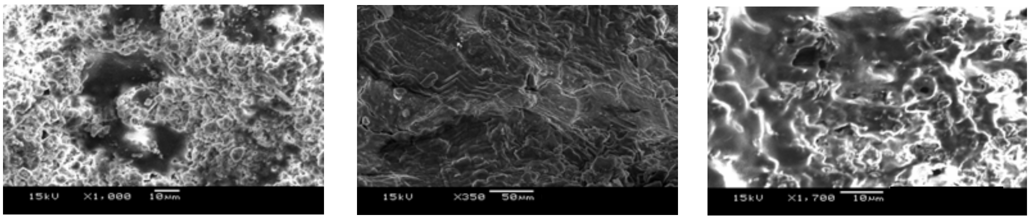


Fig (5) Shows XRD patterns of marble sample

Consolidation Process

Examination by (SEM) fig (6) shows that Rhodorsil RC 90 (5% in white spirit) was given the best result in consolidation that, it increased compressive strength with 40% and tensile strength with 39% it was given the best effect in isolation that it reduced the water absorption with 92% and porosity with 84% and it dosen't change the marble surface color. Total results seen in table No. (1).



(a) (b) (c)

Fig (6) SEM photomicrographs show the marble samples after treatment and artifical weathering. a : Wacker 290 b: Motema30 + Paraloid B72 c: Rhodorsil RC90

Table (1) shows the physical and mechanical properties of marble samples before, after treatment and artificial weathering

Property	Before	Wacker 290		Rhodorsil RC90		Motema30 + Paraloid B72	
		After	Changes (%)	After	Changes (%)	After	Changes (%)
Bulk Density gm/cm^3	2.6	2.65	19	2.8	77	2.7	38.5
Water Absorption (%)	1.2	0.6	50	0.1	92	0.95	25
Porosity (%)	1.9	0.85	55	0.2	84	1.2	37
Compressive Strength Kgm/cm^2	212.5	238.4	12	296.5	40	271.8	28
Tensile Strength Kgm/cm^2	29.7	33.86	13	41.2	39	37.7	27

Treatment and Conservation

The first stage of the treatment and conservation was to remove the dirt layer to reveal the marble surface. Loose dust was first removed with a vacuum cleaner[11] then mechanical cleaning has been carried out using manual tools. Chemical cleaning has been carried out using a solution of 100 cm^3 distilled water, 10 gm non-ionic surfactant and 1 cm^3 Ammonia then mora poultice used[12], it consists of 60 gm ammonia bicarbonate, 60 gm sodium bicarbonate, 60 gm carboxy methyl cellulose, 25 gm ethylene di-amine tetra- acetic acid, 10 gm fungicide (cetavlon) in 1 litter of distilled water. The poultice in the form of a clear jelly, is applied to a pre-wetted surface by spatula or by brush to a thickness of 3-4mm and is covered at once with thin poly ethylene film to prevent drying out and it leave for twenty four hours, then it was removed Then, the surface washed with distilled water. Stainless steel rods were used with Araldite AY 103 (20%) and marble powder to reinforce, fix and complete the disintegration parts[(13)] in the marble cenotaph of the mausoleum. Iron stains have been removed by applying a five percent solution of sodium dithionate in poultice sepiolite clay. The poultice was covered with thin film of poly ethylene for twenty four hours then it was removed.[(14)] Consolidation and isolation of all marble objects have been carried out with Rohdorsil RC 90 (5% in white spirit). Fig (7) shows the marble objects after treatment and conservation.

Fig (7) shows the marble objects after treatment

Conclusion

Deterioration of marble may be mainly attributed to the combined effects of salt crystallization and thermal changes. The most important salt species identified are halite and gypsum. The first obviously related to subsurface water while, the second is due to the air pollution. These salts cause scaling, exfoliation and powdering surfaces of marble objects. Mora poultice was given a good result in cleaning. Araldite Ay 103 and marble powder with stainless steel rods was given a good result in fixing of disintegrated parts. Rhodorsil RC 90 (5% in white spirit) was the best compound in consolidation and Isolation of marble objects of Prince Saraghatmash Madrasa.

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