

**Deterioration and Treatment Study of Archaeological Limestone Statues, Sakkara, Egypt**

S. A. Abd El – Rahim and M.K. Khallaf

Conservation Department, Faculty of Archaeology, Fayoum University, Fayoum, Egypt.

[shehataaa@yahoo.com](mailto:shehataaa@yahoo.com)[saa00@fayoum.edu.eg](mailto:saa00@fayoum.edu.eg)

**Abstract:** Sakkara is one section of the great necropolis of Memphis, the Old Kingdom capital and the kings of the 1<sup>st</sup> Dynasty as well as that of the 2<sup>nd</sup> Dynasty are mostly buried in this section of the Memphis necropolis. A group of Greco-roman limestone statues were found in front of Serapeum tomb entrance which was built at least as early as the 18<sup>th</sup> dynasty. They called "Statues of Philosophies". They suffer from different deterioration phenomena such as missing parts, erosion of stone, presence of cracks and micro cracks, disintegration of some parts, crystallization of salts and dirt. Deterioration factors were different sources of moisture, salts, wind erosion and changes in temperature. Studying phenomena and factors of their deterioration were performed by various investigations and analyses. Stone samples were collected from these statues. Study of these samples have been carried out using polarizing microscope (PLM), scanning electron microscope (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). Treatment and conservation techniques were discussed. XRD data showed that limestone consists mainly of calcite. (PLM) examination showed presence of fine-grained calcite in stone texture. (SEM) determined disintegration between mineral grains, erosion, loose of binding material, cracks and salts crystallization. Restoration techniques of the Greco-roman statues were studied, for example mechanical and chemical cleaning, consolidation, treatment of cracks, compilation missing parts and isolation of the surface to protect it against moisture using water repellent materials.

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**Key Words:** Sakkara; serapeum; Statues of Philosophies; limestone consolidation; water repellent materials.

**1- Introduction:**

Serapeum is a name usually applied to building that was associated with the cult of the Apis bulls, or the later composite God, Serapis. (Taylor, 2004). We actually know of two Serapeums, one located at Saqqara and the other in Alexandria. (Malek, 1983). The one at Saqqara was more closely related to the Apis bulls, while the Alexandria Serapeum served as a cult center of Serapis. In reality, these two complexes served very different purposes, the Serapeum in Alexandria being more Greek in origin, while the one at Saqqara was built at least as early as the 18<sup>th</sup> dynasty. This study focuses on the earlier structure at Saqqara. (Mathieson, et al., 1997). Napoleon's expedition had searched for the Serapeum in vain, but archeologist Mariette discovered the complex in 1850, in the early days of archeology. (Farag, 1975). Mariette was led to the site of the Serapeum through his discovery of traces of some of the sphinxes (over 100) lining the dorms, that were faithfully described by the Greek writer Strabo. (Dodson, 2000). In Le Serapeum de Memphis. Excavation carried out in 1852 revealed an older gallery known as the "lesser Vaults". They had similar rock hewn chambers that had contained bulls in wooden coffins. (Mathieson, et al., 1999). They dated from year 30 of Ramesses II reign down to the 22nd Dynasty. (Taylor, 2004). The burial of Apis

XIV made in the 44<sup>th</sup> year of Ramesses II reign survived intact. Throughout 1952, Mariette's work continued resulting in the discovery of a third series of smaller bull burials. (Dodson, 2000). They ranged in date from Amenophis III of the 18th Dynasty through the 19th dynasty, the earliest burials found. Here, two coffins that of Apis VII and Apis IX were also discovered intact, along with shabtis, canopic jars and amulets. One of the Apis bulls can be found in the Cairo Agricultural Museum. (Taylor, 2004). "Statues of Philosophies" suffer from different deterioration phenomena such as missing parts, erosion of stone surface, many cracks, disintegration of some parts, crystallization of salts and accumulated dirt (Fig. 1). Deterioration factors were different sources especially daily and seasonally changes in humidity and temperature degrees and wind erosion. (Fronteau, et al, 2010).

**2- Filed observation**

The statues suffer from different deterioration phenomena such as missing parts, erosion of stone surfaces, different type of cracks; macro, micro and wide deep cracks, disintegration of many parts, crystallization of salts and dirt. Deterioration factors were different sources of moisture, salts, wind erosion and changes in temperature and moisture degrees. On the other hand

they suffer from high degradation as the following: high failure, fragile and flaking off due to high moisture and crystallization of salts (Del Monte and

Sabbioni, 1986) in addition to a bad state of their conservation (Fig. 2).



**Fig (1): The place of Statues of Philosophies and its preservation status, Sakkara, Egypt**



**Fig. (2) Details of deterioration phenomena of the statues as surfaces degradation, crystallization of soluble salts, dark layers on the surfaces, vertical and horizontal deep cracks, erosion by wind effect and missing parts.**

### 3- Materials and Methods

Stone samples were taken from the statues. The investigations of the studied samples were performed using the following methods:

#### 3.1. Optical microscopy

Samples were first observed using optical light microscopy (Zies, Japan) and then the thin sections were examined using polarized transmitted light microscopy (Olympus BX41) attached with digital camera under 40 x magnifications in plane-polarised and crossed-polarised light.

#### 3.2. Scanning electron microscopy

Scanning electron microscopy (SEM) investigations of the samples were carried out by Philips (XL30) microscope, equipped with EDX micro-analytical system to obtain the total element content in the samples.

#### 3.3. X-ray diffraction

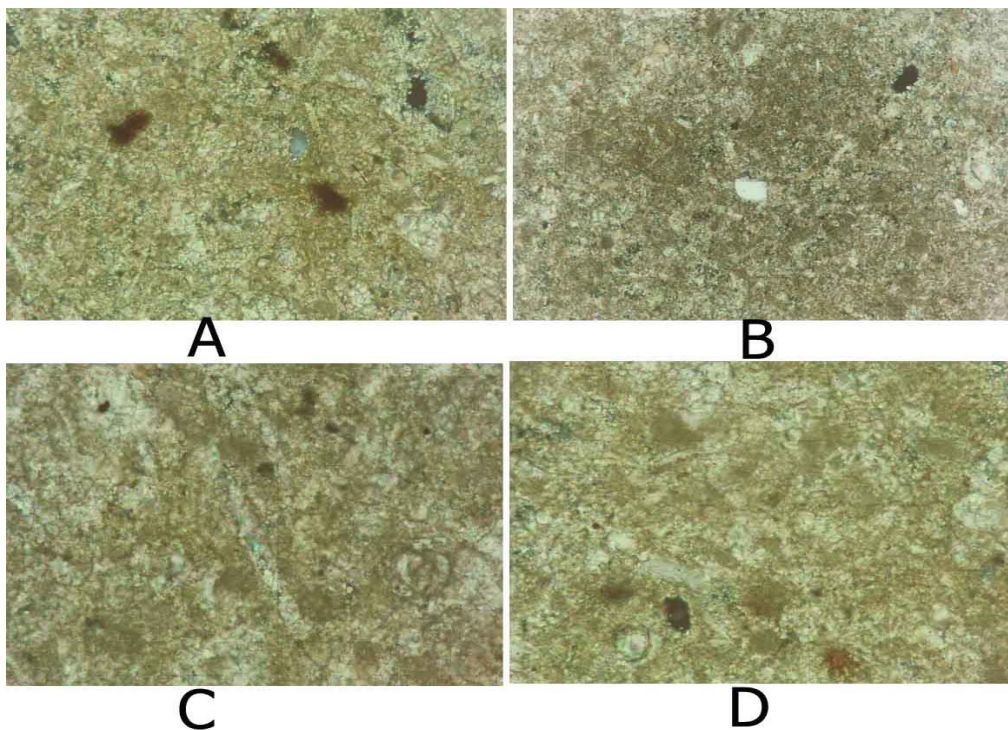
Fine powders of the samples were analysed with a diffractometer (Philips, PW 3710, CoK $\alpha$  40 kV, 30 mA).

### 4- Results and Discussion

#### 4.1 Polarizing Microscope (PLM)

Examination of thin sections of the limestone samples under plan polarised light microscope (PLM) displayed a fine-grained calcite

crystals besides presence of iron oxides, quartz, clay minerals and fossils (Fig. 3). These components increase the rate of stone decay.



**Fig (3. A-D): Shows fine grained calcite (micrite), iron oxides, clay minerals and some fine grained quartz.**

#### 4.2 Scanning Electron Microscope (SEM) equipped with Energy dispersive X-ray analysis (EDX).

SEM photomicrographs showed disintegration between calcite crystals. Loss in the binding materials between grains by the effect of salts crystallization and erosion by wind effect (Fig 4A-D).

EDX analysis was taken of the fresh unpolished cross-section. The cross-section showed the presence of calcite composed mainly of (Ca), (C), and (O). Small amounts of silicon (Si) due to quartz mineral, iron (Fe) related to iron oxides, aluminium (Al) as clay minerals, sodium (Na) and chlorine (Cl) due to presence of halite salt were found (Fig. 5). The moisture can migrate into and within a limestone sculptures in variety ways, depending on whether it is in the liquid or vapor state (Fitzner, et al., 1997) and the transformation of moisture involving variety processes, such as absorption, evaporation, diffusion and capillarity as well as the surface tension of the liquid (Inta, 1996). Furthermore presence of soluble salts within a porous material (Angeli, et al., 2010) such as limestone will increase the amount of water and there are two main mechanisms that responsible for the introduction of soluble salts into the building

including of the Statues: capillary rise of groundwater and infiltration by rainwater result in different deterioration phenomena. (Laho, et al., 2010).

#### 4.3 X-Ray Diffraction analysis (XRD)

The XRD analysis of the yellow limestone sample consists of calcite ( $\text{CaCO}_3$ ) as a major component in addition to dolomite ( $\text{Ca,Mg}(\text{CO}_3)_2$ ), and halite ( $\text{NaCl}$ ) as traces (Fig. 6). Salts can absorb moisture, especially when the relative humidity increases above their equilibrium RH. (Beck, 2010) Then, particularly the very soluble ones may deliquesce (i.e., absorb so much water vapour) that they form a saturated solution. (Charola, 1988) The term "deliquescent" is preferable to "hygroscopic" to describe this phenomenon because it identifies the condition of becoming liquid (Aneta, and Richard, 2010). The actual distribution of moisture within stone depends on porosity, pore-size distribution, and environmental conditions such as changes in temperature and effect of wind with sand. (Garland and Rogers, 1995) As discuss, the maximum of moisture content resulting from wet-dry cycling is closer to the surface in denser stones, deeper and



broader in coarse porous materials. (Beck and

Mukhtar. 2010).

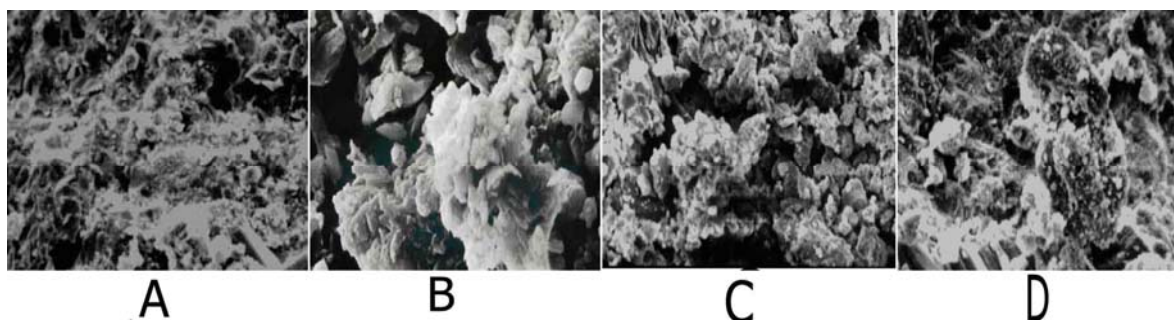


Fig (4A-D): SEM photomicrographs showing the collapse of internal structure (A), voids (B), loose of binding material (C) and salts crystallization between mineral grains of limestone(D).

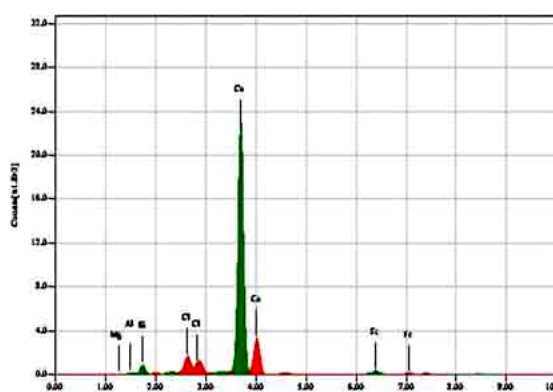


Fig. (5): EDX pattern of limestone sample

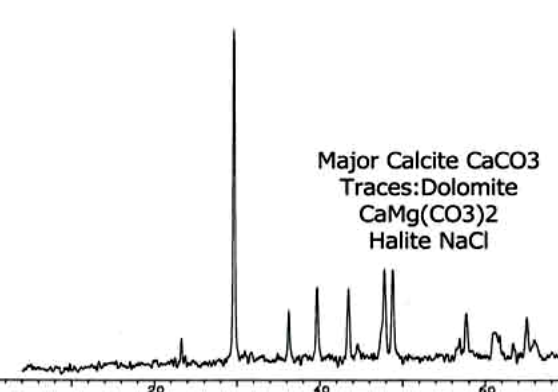


Fig. (6): XRD pattern of limestone sample

## 6- Treatment and conservation suggestions

The statues need to carry out different treatments and conservation processes which include cleaning of statues surfaces, removal and extraction of salts, stone in-fill, consolidation and water repellent treatments. These processes will be carried out as follows:

### 6.1 Cleaning Processes

The reasons for cleaning of the statues are to improve the appearance of them by removing unattractive dirt or soiling materials. (Bede, 2000). Mechanical cleaning firstly will carry out using manual and mechanical tools. Water cleaning methods are generally the gentlest means possible, and they can be used safely to remove dirt from the surfaces of the statues supplemented with non-ionic detergent; and steam, or hot-pressurized water cleaning. (Mack and Grimmer 2003). Chemical cleaners react with dirt, soiling material or paint to effect their removal, after which the cleaning effluent is rinsed off the masonry surface with water (Angeli, et al., 2010). Non-ionic detergents (which are not the same as soaps) are synthetic organic compounds that

are especially effective in removing oily soil. (Laho, et al., 2010). The addition of a non-ionic detergent, or surfactant, to a low- or medium-pressure water wash can be a useful aid in the cleaning process. Steam cleaning is actually low-pressure hot water washing because the steam condenses almost immediately upon leaving the hose. This is a gentle and effective method for cleaning stone and particularly for acid-sensitive stones. (Ana, et al., 2010). It can also be an efficient means of cleaning carved stone details and, because it does not generate a lot of liquid water. (Angeli, et al., 2010) These are usually of much the same composition as other alkaline cleaners, containing potassium or ammonium hydroxide, or tri-sodium phosphate. (Laho, et al., 2010). They are used to remove oil, latex and acrylic paints, and are effective for removing multiple layers of paint. The formulation of organic solvent paint removers varies and may include a combination of solvents, including methylene chloride, methanol, acetone, xylene and toluene. (Beck and Mukhtar2010)

### 6.2 Removal and Extraction of Salts

The most common poultice medium is clay, although paper and cotton fibers are also used, and talc, chalk and even flour are traditional poultice materials. (Laho, et al., 2010). A mixture of clay and paper fiber produces an absorbent and plastic mixture that is often favored by conservators of stone sculpture. (Aneta and Richard, 2010). This plain or true poultice is normally used for desalination, to draw out soluble salts, or as a cleaning method on substrates such as limestone that respond to water cleaning. (Angeli, et al., 2010) In these cases the poultice is allowed to dry out and the soiling and/or salts are drawn into the poultice by capillary action with the moisture (Ana, et al., 2010). Multiple applications may be necessary to draw the salts from within the surface pores. Whatever the medium, the poultice is mixed with water to form a material that will adhere to the substrate (Angeli, et al., 2010) Clay forms a sticky mass that adheres well to stone and other surfaces. These plain poultices can be conveniently mixed by hand as required on site with the addition of water to the poultice medium. (Danuta, et al., 2010).

### 6.3 Stone in fill

The mortar of stone infill for the statues missing parts and cracks treatment consists of hydraulic lime, limestone powder and sand grains (250 µm), 1: 0.25: 3 parts by wt. in order. The stone should be well matched to the original fabric in terms of color texture and finish. (Domasłowski, and Strzelczyk1993). The infill will be secured into place with stainless steel reinforcements (in large areas) and laid wet with a bedding mortar. (Gansicke and Hix, 1997). The mortar should be packed into place on a clean humid surface the mortar will be applied in successive layers not exceeding 2 cm in thickness which must cure before the new layer is applied for deep cavities stainless steel reinforcement will be used the repair will be finished with a damp sponge brush after curing. (Laho, et al., 2010).

### 6.4 Consolidation Process

Stone strengtheners based on ethyl silicates are generally applied by spraying or flooding (Clifton, 2005). Several wet – on – wet treatments are generally needed applied at intervals of 20 to 30 minutes, (Beck and Mukhtar, 2010). The exact number of treatments quantity of material and desired minimum penetration depth have to be ascertained by preliminary tests and trials. (Ana et al., 2010). The construction materials must be dry since the active in gradient in the stone strengthener, i.e., the ethyl silicates reacts with moisture. The moisture required by the stone strengthener for chemical deposition of the silica gel is supplied by the construction material

which always has a certain sorption moisture content varying in equilibrium with the atmospheric humidity. (Noll, 1986). The best working conditions are a relative humidity of 40 to 70 % and a surface temperature on the construction material of 10 to 25°C each coating operation be so arranged that the entire surface can be covered in one working day. (Aneta and Richard2010).

### 6.5 Water-Repellent Coatings

Water-repellent coatings are formulated to be vapor permeable, or "breathable". (Laho, et al., 2010). They do not seal the surface completely to water vapor so it can enter the masonry wall as well as leave the wall. Now most water-repellent coatings are water-based and formulated from modified siloxanes, silanes and other alkoxysilanes. (Wheeler, 2005). While some of these products are shipped from the factory ready to use, other water-borne water repellents must be diluted at the job site. (Mack, and Grimmer 2003). Unlike earlier water-repellent coatings which tended to form a "film" on the stone surface, modern water-repellent coatings actually penetrate into the stone substrate slightly and, generally, are almost invisible if properly applied to the statues. They are also more vapor permeable than the old coatings, yet they still reduce the vapor permeability of the stone. (Ana et al., 2010).

### 7- Conclusion

Deterioration, cracks, erosion and disintegration between mineral grains of the stone Statues occur by wind with sand erosion, moisture, changes in temperature and soluble salts migration. The investigations and analyses of samples showed that the crystalline chlorides exert a pressure on the pores which cause disintegration and cracking of stone and change it into a brittle mass in some parts. Many parts of the stone were missed. The stone contains clay minerals and iron oxides which increased deterioration of the Statues.

### Correspondence author

S. A. Abd El – Rahim  
Conservation Department, Faculty of Archaeology,  
Fayoum University, Fayoum, Egypt.  
[shehataaa@yahoo.com](mailto:shehataaa@yahoo.com)  
[saa00@fayoum.edu.eg](mailto:saa00@fayoum.edu.eg)

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