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59. P. Spathis, E. Papastergiadis, B. Christaras, M. Mavromati and M. Loukma: *Deterioration problems and preliminary observations on the conservation of the building materials of excavations of Navarino and Diikitrio, Thessaloniki.*

60. P. Storemyr: *A grinding stone quarry in the Egyptian Sahara.*

61. A. Travé and J.D. Martín-Martín: *Polishing problems in a ornamental limestone.*

62. R. H. Tykot, J. Herrmann Jr. and A. Van Den Hoek: *Survey and analysis of marble quarry sources in Algeria.*

63. C. Uhlir, M. Unterwurzacher, K. Schaller and A. Zarka: *Saxa Luquuntur: a comprensive interdisciplinary information system for antique quarries and monuments.*

64. M. C. Üstünkaya, E.N. Caner-Saltik and A.G. Gözen: *Detection of biological activity in calcareous stone by FDA analyses.*

65. A. Van Den Hoek, J. Herrmann Jr. and and R. H. Tykot: *Alabastro a Pecorella, aïn Tekbalet and Bou Hanifia, Algeria.*

66. C. Weiss, R. Sobott and I. Gerlach: *Ultrasonic and petrophysical investigations of monolithic limestone pillars at the Almaqah temple in Sirwah/Yemen.*

67. D. Wielgosz: *Provenance of marble statuary from Laodicea on the Sea (Latakia in Syria).*

68. A. B. Yavuz, M. Bruno and D. Attanasio: *A new source of Bigio Antico marbles: the ancient quarries of Iznik (Turkey).*

69. G. Zachos and E. Leka: *The ancient quarry of Pagani in Lesbos Island.*

70. C. Mas, M. A. Cau, Mª E. Chávez, M. Orfila, A. Àlvarez, I. Rodà, A. Gutiérrez Garcia-M. and A. Domènech: *Characterization of the stone used in an opus sectile pavement Pollentia (Alcúdia, Mallorca, Spain).*

DETERIORATION PROBLEMS AND PRELIMINARY OBSERVATIONS ON THE CONSERVATION OF THE BUILDING MATERIALS OF EXCAVATIONS OF NAVARINO AND DIIKITIRIO, THESSALONIKI

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From the excavations of Navarino and Diikitirio squares at the centre of Thessaloniki, large constructions of public buildings of the roman period, built during the 3[rd] AC and 1[st] BC centuries correspondingly, were found.

The problem of the conservation of the bricks and mudbricks, the main building materials of these structures, is severe and condition to select an effective preservation method is the knowledge of the composition and properties of the material, as well the processes contributing to the deterioration of the structures.

A study of the mineralogical and chemical composition and the physical and mechanical properties of the materials was carried out and from the results it follows that it consists of a mixture of silt and sand and it is mainly composed of quartz, feldspars, aluminosilicates and asbestite.

The physical and mechanical properties and characteristics, related to the weathering resistance of the materials were determined: texture, hardness, strength, bulk density, porosity, physical moisture, water absorption, sonic velocity. The results of the above measurements showed that the material is relatively stable and strength, with a great porosity, sensitive to deterioration caused mainly by water, rain and wind erosion, capillary rise of water. Preliminary experiments of conservation treatments with various organic coatings (Paraloid, silanes, silazanes, siloxanes) were carried out and the influence of these treatments to the physical and mechanical properties of the materials was measured. From the results followed that the coatings used decreased porosity and water permeability but decreased also the mechanical strength of the materials.

Deterioration Problems and Preliminary Observations on the Conservation of the Building Materials of Excavations of Navarino and Diikitirio, Thessaloniki

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ABSTRACT

In order to select an effective preservation method for the conservation of the bricks and mud bricks, the main building materials of the structures of the excavations of Navarino and Diikitirio squares at Thessaloniki, a study of the mineralogical and chemical composition and the physical and mechanical properties of the materials was carried out and from the results it follows that they consist of a mixture of silt and sand and they are mainly composed of quartz, feldspars, aluminosilicates and calcite. The material is relatively stable and strength, with a great porosity. Preliminary experiments of conservation treatments with various organic coatings were carried out and the influence of these treatments to the physical and mechanical properties of the materials was measured. From the results followed that the coatings used decreased porosity and water permeability but decreased also the mechanical strength of the materials.

KEY-WORD: Brick, mud brick, consolidation, organic coatings

INTRODUCTION

The palace complex of Galerious Maximianus was built about 300 A.C. to become the administrative and religious center of Roman Thessaloniki. The Rotonda, the Arch of Galerius, the Palace , the Octagon and the Hippodrome are it's main buildings. The southeast part of the complex is still visible. It comprises large corridors, paved with mosaics and marble slabs around a central atrium with colonnade that is surrounded by rectangular rooms. Along the east corridor four arched rooms are situated next to a large ceremonial hall with niche and mosaic floor. A monumental passage on the south led to the harbor. Founded on the spot of an older rectangular hall the Octagon is a monumental building, possibly a throne-hall, richly decorated with colorful marble slabs and paving, (Report 1997).

In the area of Diikitirio square, in the historic center of Thessaloniki, great constructions, that had been inhabited for large periods of time from the hellenistic, roman and until the byzantine times, has been found. It is a unique architectural complex in the town, that was built during the 1st B.C. century and it was destroyed from a fire during the 2nd A.C. century. The central great in dimensions building of the complex was an administrative center of the roman period of the town, (Tassia et al. 1996).

The main building materials of these structures are bricks and mud bricks, two of the earlier building materials used for thousands of years in many parts of the word.

It is known that the problems of the conservation of bricks and mainly mud bricks structures is different and mush more difficult from these of other materials of historic monuments, (Nodarou et al. 2008; Keatings et al. 2007; Goodman 2008).

Mud brick is a mixture of clay, silt and sand, mixed with water and shaped. The durability of mud brick is largely dependent on the quality of the raw material used. A durable mud brick ideally sould contain a high ratio of sand to silt and clay and not more than 10-15% clay to silt and sand. Clay and to some extent silt act as the binding media in the mixture, (Nodarou et al. 2008). The main causes of deterioration of mud brick, arising from their nature, composition and properties, are the low stability of the material due to the repeated periods of absorption-adsorption of water and evaporation of moisture, the crystalization of soluble salts at or near the surface of the structure, the destructive action of rainwater and groundwater, (Keatings et al. 2007; Skoulikidis 2000). Various non destructive methods are used for the study of the decay of the building materials of the monuments (Moropoulou et al. 2000; 2002; Christaras 1998)

In the recent past a large number of materials have been proposed as consolidants for the various types of the buildings materials of the historic building and monuments, stones, bricks, mud bricks, marbles. But it should not be assumed that a consolidant effective at one site will prove equally effective at another site where the environment, type of material, mechanism and degree of decay are different. Among other materials alkoxysilanes, alkaline earth hydroxides (calcium hydroxide in particular) are widely used on non-calcareous or limestones correspondingly materials. Also orthosilicic acid esthers (mainly ethyl silicate), having a very low molecular weight and viscosity and therefore easily penetrating into the pores of the materials, are used in various types of porous building materials, (Tsakalof et al. 2007; Favaro et al 2006).

In the case of marbles the main mechanism of deterioration is the sulfation of their surfaces, leading to the formation of gypsum layers, due to the solid state diffusion of Ca^{2+}. A consequence of this mechanism is that the protective coatings, that were not designed to retard or annul this diffusion, accelerate the sulfation. So methods of protection using coatings of epoxy or acrylic vehicle with n-semiconductors as pigments or nanocomposites coatings are also applied (Skoulikidis 2000; Giavarini et al. 2008; Liu and Zhang 2007).

Condition to select an effective preservation method against the deterioration of these materials is the knowledge of theirs composition and properties, as well the processes contributing to the decay of the structures. Aim of the present work is the study of the chemical and mineralogical composition, the determination of the physical and mechanical characteristics of the building materials of the constructions of Navarino and Diikitirio excavations of Thessaloniki and the influence on these of the application of various conservation treatments.

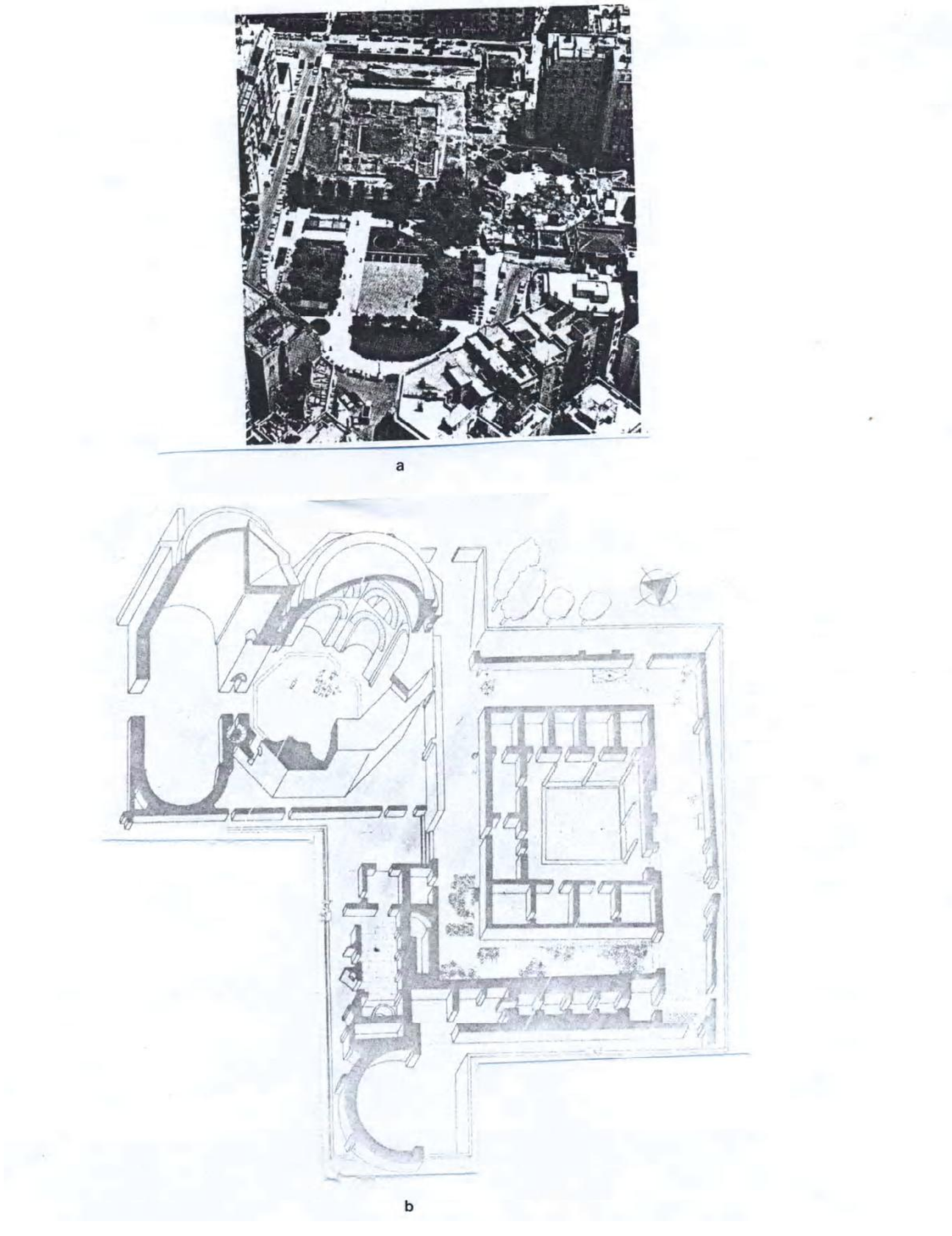

Figure 1. Navarino excavations, a) general view of the complex, b) Palace complex-reconstruction. .

Figure 2. : Diikitirio excavations, general view

EXPERIMENTAL

Series of samples collected in four different locations, $N_{1,}$ $N_{2,}$ $D_{1,}$ $D_{2,}$ were examined. N_1 and N_2 are samples from brick and mud brick correspondingly of Navarino excavations and D_1 and D_2 are samples from brick and mud brick correspondingly of Diikitirio excavations.

The chemical analysis of the samples was carried out by the Energy Dispersive Spectrometer (EDS-LINK AN 10/55S) of the Scanning Electron Microscopy (SEM) and the mineralogical analysis by X-R Diffraction (Philips diffractometer, CuKa radiation, Ni filter, $2\Theta=3^o$-53^o, with ASTM cards of the International Centre for Diffraction Data).

The follow physical and mechanical characteristics have been studied, (Kantiranis et al 2001; Christaras 1998;, Vasconcelos et al. 2008) : particle size distribution, permeability, moisture content, porosity, the point load index (Is) and the uniaxial compressive strength (UCS), ultrasonic velosity (V), Young's modulus (E).

The conservation treatment experiments were carried out with seven different organic coatings on both brick and mud brick samples. The criteria for the selection of these coatings was to be representative of the various types of the organic compounds used and the informations about their behavior in various cases of building materials and deterioration problems. Experiments on the following samples were carried out, uncoated (0) or coated (1-7) with the corresponding compounds, all of these as 5% solutions in toluene. The application of the coatings on the samples was carried out by the compress method (with paper-pulp immersed in the corresponding solution).

0) Uncoated sample
1) Paraloid B-48
2) Paraloid B-72
3) Octamethyl-cyclo-tetrasiloxan
4) Octamethyl-trisiloxane
5) Hexamethyldisiloxane
6) Teteramethylsilane
7) 1,1,1,3,3,3, Hexamethyldisilazane

RESULTS AND DISCUSSION

The results of the chemical and mineralogical analysis of the samples are shown in Tables 1 and 2.

Table 1.Chemical composition (%) of the samples

Compound	N_1	N_2	D_1	D_2
Al_2O_3	19.08	14.21	13.03	15.49

FeO	10.02	3.87	9.95	11.09
SiO_2	53.94	51.76	48.74	44.25
K_2O	2.36	1.70	1.89	2.46
MnO	0.30	0.16	0.49	1.15
MgO	5.21	9.98	3.10	4.01
Na_2O	0.93	0.80	1.43	0.84
P_2O_5	0.35	2.23	1.23	1.17
TiO_2	0.67	0.30	1.45	0.71
CuO	0.32	0.21	-	0.09
ZnO	0.18	0.46	0.17	0.16
CaO	5.54	12.24	14.30	14.45
SO_3	0.11	0.96	1.57	2.47
Cl	-	-	-	-
Hg	0.02	0.29	-	0.04
PbO	0.02	-	-	0.05
Loss of ignition	0.98	0.86	2.68	1.57

From these results follows that the materials of the two constructions are similar. The samples from Navarino are mainly composed of quartz, aluminosilicates, calcite, whereas these from Diikitirio contained also and feldspars. The samples of the brick of both constructions contained 55% quartz, whereas the samples of mud brick, of both also constructions, contained a lower percentage of 35% quartz.

The particle size distribution shown in Figure 3 indicates that the material is composed from 75% silt and 25% sand.

Table 2. Mineralogical composition of the samples

N_1

Mineralogical composition	Semiquantitative composition (%)
Plagioclaste	Plagioclaste 31%
Zoisite	Zoisite 9%
Quartz	Quartz 54%
Calcite	Calcite 6%

N_2

Mineralogical composition	Semiquantitative composition (%)
Moscovite	Aluminosilicates 33%
Amphivole	Pyroxene 5%
Pyroxene	Amphivole 7%
Plagioclaste	Quartz 34%
Quartz	Plagioclaste 16%
Talc	Calcite 5%
Calcite	

D_1

Mineralogical composition	Semiquantitative composition (%)
Pyroxene	Pyroxene 8%
Quartz	Quartz 57%
Feldspars	Feldspars 30%
Zoisite	Zoisite 5%

D_2

Mineralogical composition	Semiquantitative composition (%)
Chlorite	Aluminosilicates 37%

Moscovite	Calcite 6%
Feldspars	Feldspars 22%
Quartz	Quartz 35%
Calcite	

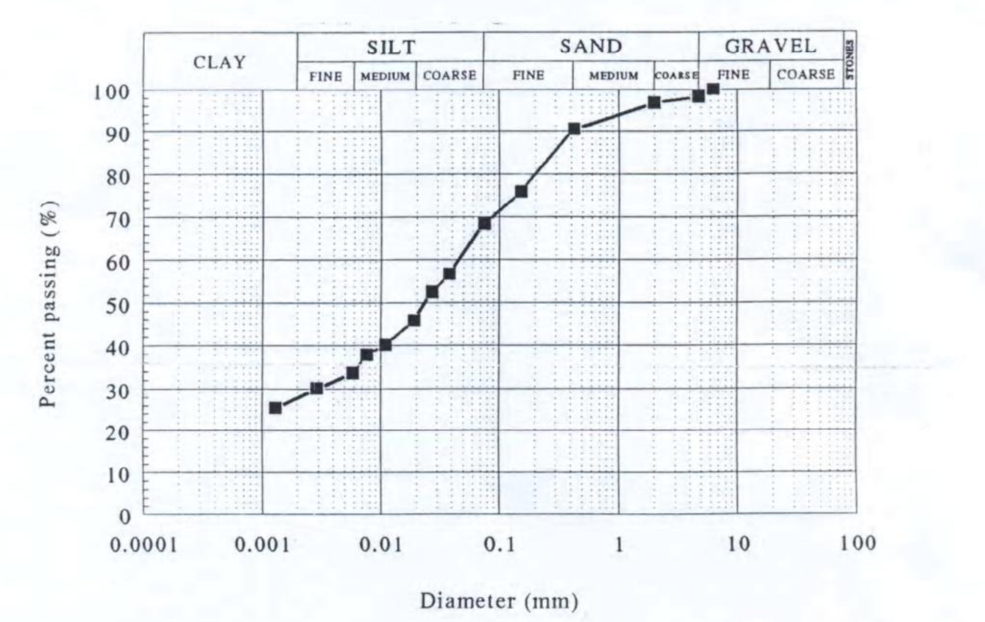

Figure 3. Particle size distribution of samples

The values of the physical and mechanical characteristics of the material, untreated or treated with the various coatings used, are shown in Table 3.

Table 3

Physical and mechanical characteristics of samples.

a) brick

	0	1	2	3	4	5	6	7
Bulk density, γ (gr/cm^3)	2.19	1.95	1.93	1.92	2.01	2.15	2.04	2.15

Permeability factor, k (cm/s)	$3x10^{-3}$	$2x10^{-4}$	$1x10^{-3}$	$5x10^{-4}$	$8x10^{-4}$	$2x10^{-5}$	$7x10^{-4}$	$9x10^{-4}$
Porosity, n	32.3	26.6	30.5	28.2	28.6	23.1	27.6	21.4
Point load index, Is (MPa)	7.5	6.2	6.9	6.3	5.2	5.7	5.5	5.5
Uniaxial compressive strength, UCS (MPa)	134	108	124	115	97	106	104	104
Ultrasonic velocity, V (m/s)	1662	1752	1846	1907	1827	1783	1839	1791
Young's modulus E (MPa)	4.47	3.73	4.16	3.76	3.16	3.46	3.34	3.31

b) mudbrick

	0	1	2	3	4	5	6	7
Bulk density, γ (gr/cm^3)	1.81	1.73	1.58	1.59	1.60	1.59	1.62	1.77
Permeability factor,	$7x10^{-5}$	$2x10^{-5}$	$1x10^{-5}$	$3x10^{-6}$	$7x10^{-6}$	$2x10^{-6}$	$9x10^{-6}$	$5x10^{-6}$

k (cm/s)								
Porosity, n	35.5	16.5	13.5	31.8	30.6	31.5	30.8	14.3
Point load index, Is (MPa)	*	*	*	*	*	*	*	*
Uniaxial compressive strength, UCS (MPa)	**	**	**	**	**	**	**	**
Ultrasonic velosity, V (m/s)	1751	1287	1398	1213	1430	1372	1961	1931
Young's modulus E (MPa)	***	***	***	***	***	***	***	***

* All values<1.8 MPa

** All values<32 MPa

***All values<1.14 MPa

The results of the chemical, mineralogical composition and the physical and mechanical characteristics of the untreated material show an absence of clay and a high ratio of silt to sand that cause a dimensional instability of the structure (Nodarou et al. 2008; Keatings et al. 2007), whereas the low presence of soluble salts does not influence significantly its behaviour, (Moreno et al. 2006; Carta et al. 2005). The observed great values of porosity in combination with the low permeability and the above mentioned nature of the material indicate that the water can easy penetrate and remain into the material, resulting in a destructive influence of the rain water due to the absorption and evaporation of the moisture that causes changes in the volume and cracks in the bulk and the surface of the structure, leading to deterioration, (Simao et al. 2006; Sharma et al. 2007).

The results of the physical and mechanical characteristics of the treated materials (Table 3) show that all coatings used in both brick and mud brick samples decreased porosity and water permeability, this decrease been greater for the mud brick samples. In the case of brick better results are shown for the Hexamethyldisilazane coating (sample No 7), whereas in the case of mud brick better results were obtained for the Paraloid B-72 coating (sample No 2). But the application of the coatings decreases also in all cases the mechanical strength of the materials, as shown from the corresponding values of the results of Table 3.

Further experiments must be carried out to explain this behavior, study the corrosion resistance of the treated materials and find out a method of treatment that will improve all characteristics and properties of the materials, protecting against deterioration.

CONCLUSIONS

1. The building materials of the constructions, brick and mud brick, consist of a mixture of silt and sand and they are mainly composed of quartz, feldspars, aluminosilicates and calcite.

2. The results of the study of the physical and mechanical properties and characteristics of the materials showed that the materials are relatively stable and strength, with a great porosity, sensitive to deterioration caused mainly by water, rain and wind erosion, capillary rise of water.

3. Experiments of conservation treatments with various organic coatings (Paraloid, silanes, silazanes, siloxanes) were carried out and the influence

of these treatments to the physical and mechanical properties of the materials was measured. From the results followed that the coatings used decreased porosity and water permeability but decreased also the mechanical strength of the materials.

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