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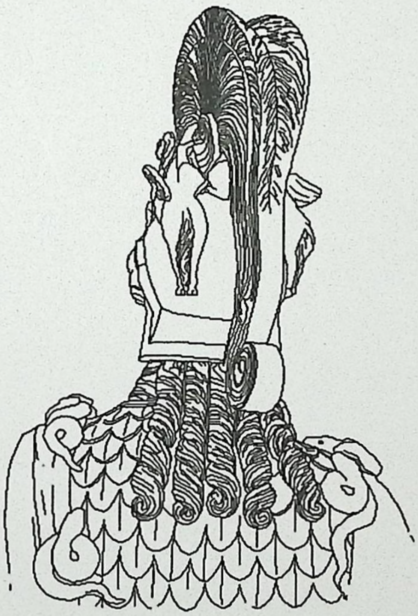

CORROSION FORMS AND CONSERVATION TREATMENTS OF THE ATHENA (MINERVA) STATUE OF THE ATHENS ACADEMY - GREECE

V. LAMPROPOULOS et alii

CONSERVATION AND RESTORATION OF THE ARCHAEOLOGICAL SITE OF KOTZIA SQUARE, ATHENS - GREECE

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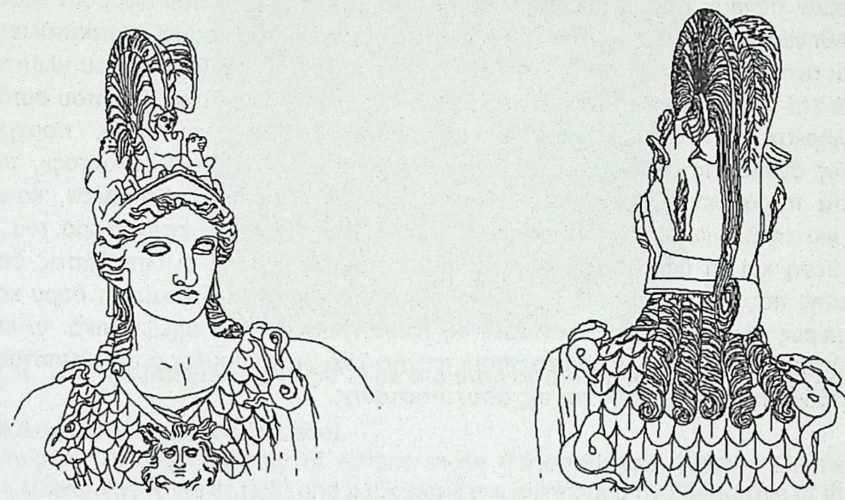


CORROSION FORMS AND CONSERVATION TREATMENTS OF THE ATHENA (MINERVA) STATUE OF THE ATHENS ACADEMY – GREECE

V. LAMPROPOULOS, D. KOUTROMANOU, D. PAPAGEORGIOU, A. TSORONI & P. TZANOULINOS

LAMPROPOULOS V.*, 64 - 66 Pandosias str., Athens 11142, Greece.
e-mail: blabro@teiath.gr
website: www.vlampropoulos.gr
KOUTROMANOU D., Vironos 11, Agia Paraskevi, Athens, P.C.15343.
email: dkoutromanou@yahoo.gr
PAPAGEORGIOU D., Alexandras 107, Ampelokipi, Athens, P.C.11472.
email: flopsssy@hotmail.com
TSORONI A., 9 Vergi str., Zografou 15772, Greece.
e-mail: atsoroni@yahoo.gr
TZANOULINOS P., 29 Pindou str, Argyroupoli 16451, Greece.
e-mail: praxis_tzanoulinos@yahoo.gr

*Author to whom correspondence should be addressed.

ΠΕΡΙΛΗΨΗ

Το παρόν πόνημα αφορά την παράθεση ιστορικών στοιχείων που αφορούν τόσο το κτίριο της Ακαδημίας Αθηνών όσο και το άγαλμα της Αθηνάς Προμάχου που κοσμεί τα προπύλαια. Εν συνεχεία περιγράφεται αναλυτικά η κατάσταση διατήρησης και οι μορφές διάβρωσης του γλυπτού, της βάσης και του κίονα επί των οποίων εδράζεται καθώς και των μεταλλικών στοιχείων που αυτό φέρει. Για να καταστεί πληρέστερη η μελέτη και να κατανοηθεί σε βάθος το υλικό, πραγματοποιήθηκαν φυσικοχημικές αναλύσεις στο εθνικό ερευνητικό Ίδρυμα Ε.Κ.Ε.Φ.Ε. «Δημόκριτος», των οποίων τα αποτελέσματα παρατίθενται και σχολιάζονται στο σχετικό κεφάλαιο. Επιπλέον, καταγράφονται οι επεμβάσεις για τη βελτίωση της στατικότητας που στόχο έχουν την επαναφορά του γλυπτού στην αρχική του θέση και τη διασφάλιση αυτής. Τέλος, παρουσιάζονται οι επεμβάσεις συντήρησης και αποκατάστασης που πραγματοποιήθηκαν στο γλυπτό, τη βάση, τον κίονα, το δόρυ και την ασπίδα. Σημαντικό μέρος της εργασίας αποτελεί το φωτογραφικό και σχεδιαστικό υλικό, μέσω του σχεδιαστικού προγράμματος autocad το οποίο τεκμηριώνει με λεπτομέρεια την κατάσταση διατήρησης και όλα τα στάδια της συντήρησης και της αποκατάστασης.

ABSTRACT

This paper relays the history of both the building of the Academy of Athens and the statue of Athena Promahos that adorns the Propylon. Additionally, it describes in detail the maintenance state and the forms of corrosion of the sculpture, the base and the column on which it abuts, as well as the metal elements that it bears. In order to fully comprehend the material to be preserved, physicochemical analyses were carried out in the National research institution "Dimokritos". Moreover, the interventions for the static improvement of the sculpture have been meticulously recorded. They concern the placement of the sculpture in its initial position and the measures taken to secure it there. Finally, the conservation and restoration treatments of the sculpture are presented as well as those of the base, the column capital, the column, the spear and shield of Athena. Elements regarding the mechanical and static sufficiency of the statue are also included. Large part of this project consists of both drawings on the designing program autocad, and photographs, which document in detail the preservation state and all the subsequent conservation and restoration interventions.

HISTORICAL OUTLINE

1.1 History of the Athens Academy

The building of the Athens Academy (Fig. 1) is one of the three buildings of the 'architectural trilogy' in the city centre of modern Athens: National Library - University - Academy.

The donation of baron Simon Sinas in 1856 played a crucial role in the promotion of the idea of the Academy Foundation. His donation entailed the construction of the sculpture and painting decoration of the neoclassical palace that today houses the Athens Academy (28). To this end, Simon Sinas commissioned an architect who would best serve his vision. His name was Theophil Hansen (1813-1891). Hansen chose pentelic marble to be the structural material of the building. In 1868 Hansen chose the sculptor Leonidas Drosis (1843-1884) to execute the sculptural decoration of the Academy megaron (palace). The Athens Academy was dedicated on the 18th of March 1926, thirty nine years after the delivery of the building in 1887, by the Prime minister Harilaos Trikoupis, as the Academy of Sciences, Intellect and Fine Arts.

Fig. 1. The 'architectural trilogy'. The building of the Academy is in the red frame.

1.2. The Academy megaron (palace).

The monument of the Academy of Athens faces Panepistimiou Avenue. On its left side it borders Athens University, while its right and back sides are enveloped by the garden of the Academy, which extends north up to Academy Avenue and east to Sina street.

The building is constituted of the central department and two wings, and has features of the Ionic order (11) (Fig. 2). The megaron of the Academy has a rich sculptural decor, which was executed between the middle of the 1870s decade and the end of the 1880s decade. The larger part of this decor is work by the sculptor Leonidas Drosis (1843-1884) (18). The two statues, Athena Promahos (Fig. 3), height 4.11 m and Apollo, height 3.75 m., are also works by Drosis. They have been placed on two columns of Ionic order, of total height 18.98 m, on the right and on the left of the building entrance (12). These statues, that adorn the facade of the academy, are both symbols of culture and leading intellectual examples.

Fig. 2. Illustration of the Academy building in the beginning of the 20th century.

1.3. Athena Promahos - Historical elements in regard to the goddess.

Goddess Athena (also named Minerva by the later Romans), the personification of wisdom and the arts, was described as "Promachos" because she helped humans in battle and stood by their side in difficult times. The figurative type of Promachos was created in the 6th century B.C., in the years of tyrant Peisistratus, after the reorganisation of the feast of Panathinaia. Athena is sometimes seen to wave her spear in the battle, while other times she appears calm, resting, with her spear lowered. In Greek mythology, Athena is always a tough opponent to her enemies. However, unlike Eris (later named Mars by the Romans), Athena does not find pleasure in battle. She rather prefers the regulation of differences by applying the law with peaceful means. In times of peace, Athena does not keep weapons, and, should she need any, she borrows from her husband, Zeus. Nevertheless, she never loses a battle, not even against Eris himself, since she has better tactics and strategy. The prudent leaders and warlords always resort to her advice (3).

Fig. 3. Statue of Athena.

General information about the statue: Hologlyph statue placed on column of Ionic order, holding cupreous shield and spear. The material is pentelic marble. It is placed in the Propylon of the Academy of Athens, Attica, Greece. The dimensions are: maximum height (without the column and base): 4.11 m. Total height (statue, column and base): 23.25 m., maximum width of statue (without column and base): 1.73 m. and maximum width (with column and base): 4.87 m.

Detailed description: The statue is placed on a column of Ionic order, on the right of the building entrance. It represents a feminine form in standing position, with the head turned slightly to the left and the torso facing the spectator. It is placed on a square base. The left leg is slightly bent. In the left hand she keeps a shield decorated with the head of Medusa, while in the right she keeps a spear. The helmet is decorated with two winged horses on either side. The figure wears a long square veil, together with a goat's skin and a parapet of armour, cloak and sandals. The column capital consists of an abacus, which is decorated with spiral helixes of undulated lines; a colarin, with sculptural decorative elements; and the base, whose striations follow those of the column trunk. The column is thin, with horizontal striations and narrows lightly towards the top. The base is constituted of a large diameter ring that rests on three square steps.

2. PRESERVATION STATE

The deteriorations that have been observed on the pentelic marble and the other manufacture materials of monuments are owed to the individual or combined effects of environmental conditions, engineering, physicochemical and biological factors, in combination with both the chemical structure of marble, and human interventions.

The following deteriorations have been observed on the Athena statue:

- "Carbonisation" of the surface areas that are exposed to rainwater.
- Sulfation in surface areas that are not exposed to rainwater.
- Cracks - fractures - discontinuities of marble caused by the oxidation and inflation of iron contacts, as well as from the mineralogical heterogeneity of marble (discontinuities of marble and mechanic strain e.g. earthquakes) (Fig. 4).
- Wetting and exfoliation have occurred in areas where the marble presents decreased cohesion, infiltration and withholding of increasing quantity of water.
- Deposition of particles - black crust is located in areas that remain protected from rainwater causing undesirable aesthetic effects. This phenomenon is mainly observed in areas where the marble surface has deteriorated and the porosity has increased, which results in hovering particles penetrating more easily the material (Fig. 5).

marble surface has deteriorated and the porosity has increased, which results in hovering particles penetrating more easily the material (Fig. 5).

• Deterioration caused by metal elements (iron, copper, lead) that cause chromatic alteration of marble and small cracks from metal oxides. Erosion of iron laminas had been located in the gap between the base and the top of the column capital. This had caused the sculpture to move from its initial place, which resulted in static problems and cracking.

• Deterioration caused by biological factors. Birds' excretions wear out the surface of the material, while at the same time creating an undesirable aesthetic effect.

• The human factor in deterioration. The steps in the base of the column were covered in graffiti and the colours had penetrated the marble pores.

• The results of vibrations. There has been dislocation of the statue and its base. The main cause of this phenomenon was the vibrations resulting from sounds, noises and earthquakes. The greatest deterioration has been caused by seismic vibrations (locomotion and intensity of cracking).

• Previous conservation interventions. These were observed in the cracks and in the discontinuities of the marble, which had been sealed with silicone. Moreover, in previous attempts of strengthening the support of the shield, grey cement and iron elements had been used, as seen in Fig. 6. What is more, it is likely that the manner of support of the spear had been altered by introducing a metal joining, which had been fixed on the cloak of the sculpture.

Fig. 4 Cracks due to the mineralogical heterogeneity of the marble.

Fig. 5. Deposition of particles.

Fig. 6. Previous intervention for the support of the shield using grey cement and iron elements.

3. PHYSICOCHEMICAL ANALYSES

The samples were observed in a petrography microscope, in reflected light (Fig. 7), so that we could get a first idea of their morphology. Analyses were subsequently performed via two spectroscopic techniques: scanning electronic microscope (S.E.M.) and analysis of spectra of X-Ray Diffraction (X-R.D.).

Fig. 7. Magnification 4,5 in point of sample 1.

3.1. Samples' analyses via S.E.M..

Location of samples analyzed with S.E.M:

- Mortar between the base of statue and column capital.
- Discontinuity of marble from the body of the statue.
- Black crust from the base.
- Colour traces from column.
- Black crust from the cloak of Athena.
- Metal element from the base of Athena.

Typical diagram of analysed sample.

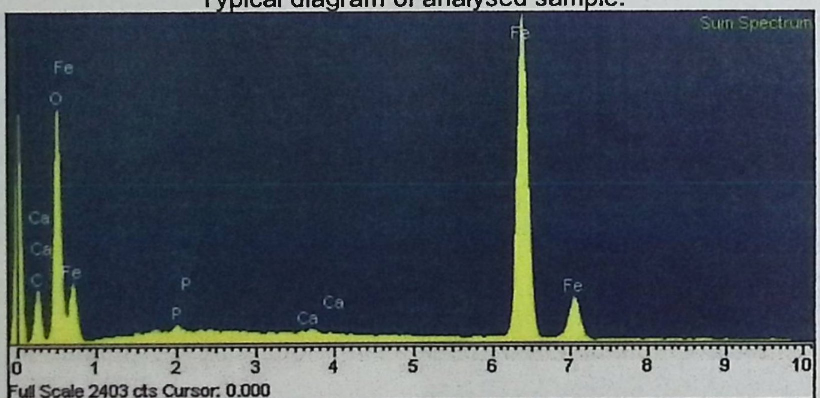


Diagram: Element peaks of the sample.

Observations: It is iron with calcium depositions (most likely the product of iron oxidation) and phosphor (most likely from excrements of birds) in points.

Observations for the rest of the analysed samples:

1. The elements found are mainly calcium, oxidised iron and sulphur. These indicate the formation of the black crust on the marble.
2. This analysis was performed on a sample of colour, which contains mainly barium white and iron oxides.
3. Incisions on the marble were found covered in iron, sulphur, calcium and aluminosilicates components.
4. This analysis was performed on a sample of colour consisted mainly of lead red, chromium and barium white.
5. The black crust analysed on this area of the marble was found to contain calcium, sulphur, iron and silicon.

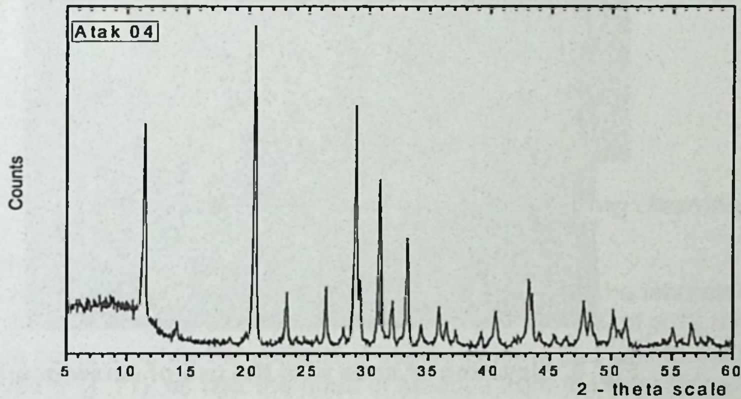
6. In this area the analyses showed high concentration of lead (most likely because of the leading). The colour contains oxides of iron and lead.
7. In this sample the peaks indicate the aluminosilicates components.
8. This analysis presents marble and mortar (calcium, sulphur, silicon, iron and chloride, most likely from ions of chloride).
9. Area of 'healthy' marble (it does not contain aluminosilicates components).
10. Area of sulfated marble (presence of sulphur and silicon).

3.2. Samples analyses via X-R.D..

Location of samples analyzed with X-R.D.:

- Black crust from the cloak of the statue.
- Corroded veins/grains from the cloak on the Eastern side.
- Black crust with colour from the decorative elements of the column capital.

Typical diagram of analysed sample.



The peaks correspond to gypsum (gypsum: 33-311) and the peak in the 140 corresponds to chloride lead (Pb-chloride: 25-434) or chloride calcium (Ca-chloride: 16-119).

Conclusions: The existence of gypsum (it was located in all the 3 samples) confirms the 'Carbonisation' of the marble surface. Tracing of quartz indicates the existence of venations with aluminosilicate components.

4. CORROSIONS FORMS

Factors of stone deterioration:

1. Stone corrosion because the effect of water
2. Capillary rising of humidity from the ground
3. Infiltration of rain waters
4. Condensation of atmospheric humidity
5. Stone corrosion from frost
6. Stone corrosion from the effect of water in aluminosilicates components - Inflation of clays - Thixotropy
7. Ionexchange deterioration of aluminosilicates mining
8. Stone corrosion from soluble salts
9. Stone corrosion because of the atmospheric pollution
10. Stone corrosion from the existence of metal contacts
11. Stone corrosion from mechanic strain caused from temperature changes
12. Biological deterioration factors
13. Humans as a deterioration factor
14. Previous interventions
15. Corrosion of iron elements
16. Corrosion of cupreous elements

5. INTERVENTIONS FOR THE STATIC IMPROVEMENT

5.1. Placement of titanium bars.

This intervention aimed at the reinstatement of cohesion of the statue's parts, the evasion of future detachments and the mechanic welding of individual parts. Ribbed titanic bars of diameter 12 mm and length 85 cm, with bent 2%, were placed horizontally, in order to avoid hitting on another bar.

5.2. Turning and relocation of the statue.

This intervention aimed at the static improvement of the statue and the restoration of its initial place. More specifically, the marble decorative elements were abstracted from the mottle body, as was the lead in the gap between the base of statue and upper part of the column capital.

Afterwards a metal frame was manufactured and placed around the upper part of the column capital, where a piston was installed for the locomotion of the statue. A slight elevation was achieved with the use of a screw gear (Fig. 8), while suitable gentle pressing was applied with the use of a piston, supported in the metal frame, near each edge of the base. The process was repeated three times until the desirable result had been achieved.

Fig. 8. Elevation of base with the use of screw gears.

5.3. Replacement of iron elements.

This intervention aimed at the restoration of resistance of the base and the replacement of corroded elements. Screw gears, aiming at the elevation of base, were used for the replacement of iron wedges, with lead- invested stainless steel of the same dimensions.

5.4. Restoration of the gap between base and column capital.

This intervention aimed at the aesthetic restoration, the sealing of the gap for reasons of preventive maintenance, and the static restoration of statue. For the restoration, lead leaves were used as fillers to the gap, while new decorative elements were applied on the marble.

6. WORK ON THE SHIELD AND THE SPEAR

6.1. Removal of shield from the statue.

The shield was isolated from the left hand of the statue with the removal of metal elements that connected it to the shoulder and the palm (Fig. 9). A metal frame, securing the shield in four points, was introduced. The transfer was carried out by a crane, placing the hook in the ring of the metal frame. Then the shield was placed in the central hall of the Academy where photographic documentation, design imprinting and conservation treatments took place.

Fig. 9. Removal of metal elements that connected the shoulder to the shield.

6.2. Conservation treatments.

The cleaning of the shield was done mechanically with the use of a lancet on the very hard crusts, Dremel with brushes of cupreous fibres on the bigger surface and iron fibres locally, commonly on surfaces with products of erosion (Fig. 10). The cleaning of the surface from dust and dissolved products of erosion was done with acetone solvent. The completion of cleaning was followed by the protection of metal surfaces with microcrystalline wax b-square 193[1,2]. The next step concerned the packing of the shield in bubble wrap, for its safe transportation to the metal working laboratory.

Fig. 10. The head of Medusa on the shield, during cleaning.

6.3. Metal working laboratory.

37 iron dowels, with a diameter of 10 mm each, were removed in the laboratory. These dowels had been placed at a distance of 12 cm from each other. 7 more dowels, of a 12 mm diameter, were also removed[3]. The iron hoop, which is the support of the cross arms that was found at the back of the shield, was also removed (Fig. 11), as was the head of Medusa from the front side of the shield. After these removals, cleaning was performed at the points where the iron elements existed and at the back side of the head of Medusa. The cleaning of the surface from dust and dissolved products of erosion was done using solvent of acetone. The cleaning was followed by the replacement of the iron elements with brassy elements of corresponding dimensions (Fig. 12), with the exception of the new brass dowels that were all of a 15 mm diameter. Afterwards, the head of Medusa was fixed in its original place on the shield. This was followed by the process of protection of the metal surface with microcrystalline wax b-square 193. Lastly, and as part of the aesthetic restoration, in order to minimise the shine of the new brass elements, the pieces were covered with a solution of artificial oxidation for copper which creates black patina.

Fig. 11. The back side of the shield before cleaning.

Fig. 12. The back side of the shield after cleaning.

[1]After the cleaning of the surface with solvent of acetone and hydric cotton, the surface was warmed up with pilot light propane until the temperature of the metal surface reached 100 °C.
[2]The solution of wax was 10% w.v. in solvent white spirit, and was created by heating the solvent in a fire-retarding glass container. Afterwards the solution of wax was spread on the surface 2 - 3 times, with a paintbrush.
[3]With the tools punch and hammer the heads of dowels were marked (staking), so the drill would be steady in their circular surface.

6.4. Re-laying of the shield.

The shield was packed with bubble wrap and was transported to the Academy where it was placed again on the sculpture with the help of a crane. More concretely, the five support pins that retained the shield on the statue, and the grey cement that used to hold them in place, were replaced with brass pins and were fixed on the statue with mortar[4].

6.5. Spear's manufacture description and conservation/restoration.

The spear is constituted by two cupreous parts: the forward and back part. These were probably screwed in an iron contact which is found in the right hand of the statue and connects the marble with the spear. Initially, it was attempted to abstract the shied in two parts. This was rendered impossible, as there was great danger of fracturing the marble of the statue. Afterwards, the iron support of the lower part of the spear was removed, which was replaced with bronze and was fixed with mortar[5]. Also, the iron counterpoise from the back part of spear was removed (Fig. 13) and was also replaced. The new counterpoise is bronze and cast in mould.

The spear was cleaned mechanically with Dremel and a bronze brush. Artificial patina was applied on the surface of the brassy and bronze elements, for both aesthetics reasons and the protection of copper.

Fig. 13. The iron counterweight.

7. CONSERVATION AND RESTORATION WORK

7.1. Cleaning.

The black crust was initially removed from the superior layers of the marble with the use of a Dremel wheel[6] on a very low speed. Afterwards, an ultrasound tool was used, in average intensity level of 3 - 4. In the all remainder surface, for the removal of the deposits and atmospheric pollutants, the cleaning was done with use of wet grit blasting of low pressure, in combination with mechanic tools. For the comparison of the cleaned surface with the initial, as well as for the keeping of data for potential future research, an area of black crust 3x4 cm, was left uncleaned at the base of the statue. For the maintenance of the red colour remains, mechanic cleaning with a lancet was performed, in order to decrease the amount of black crust. This was followed by cleaning with an ultrasound tool in low intensity (1 - 2), for the evasion of likely peeling. Pasta Mora[7] was also used for the facilitation of black crust removal (Fig.14). Humid cleaning was carried out at the column, in combination with low-pressure air and steam. Additionally, mechanical cleaning was done at points where hard deposits and black crust had been located. The steps at the base of the column were also cared for with humid cleaning in combination with mechanic cleaning and the use of steam. The graffiti pigments were removed with chemical solutions: graffiti remover, nitro uprs (unsaturated polyesteric resins) and acetone.

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[4]Mortar composition: 25% white cement, 25% quartz sand, 50% marble powder. A resin for cohesion of mortar, with the commercial name "REVINEX", was also added to the mix.

[6]Whet conical, cylindrical and round form stones were placed on the peak of the wheel, from aluminium oxide 9,5 mm in executive 3,2.

[7]Constitution of pastry Mora: H_2O: 100 cc, carbonic salt of ammonium NH_4HCO_3: 6 gr, EDTA: 2,5 gr, Desogen: 1gr and carboxymethylcellulose (or neutral paper): 6 gr. The time of action and the density of pastry were differentiated depending on the type and the thickness of the deposits (crust).

Fig. 14. Cleaning for the removal of black crust.

7.2. Sealing.

After removing the remains of silicone from previous interventions, sealing was done all over the surface of the statue[8], at the places that cracks and micro-cracks had been located. At the column and the column capital, sealing of cracks was done with mortar of the same constitution.

7.3. Consolidation.

The consolidation of the statue and the column capital was done in two stages. Before the processes of conservation, 30 sprayings with saturated solution of calcium hydroxide ($Ca(OH)_2$) were performed as part of the pre-consolidation process, so that the surface would become more stable and durable to the interventions of conservation that would follow. Afterward consolidation, 50 more fixing sprayings were also performed with calcium hydroxide. The application of fixing and pre-consolidation sprayings was done 3 times daily. Pre-consolidation sprayings were not applied on the surface of the column; however, 80 fixings with calcium hydroxide were applied after the conservation interventions, with the same frequency of application.

7.4. Adhesion.

A part of the north-eastern helix of the column capital, which had been detached, was adhered with mortar[9]. Moreover, two titanium bars were placed in the north-western column capital. More specifically, two holes were opened with a rotary drill, while the detached marble piece "locked" in its original place. The piece was then removed and cleaned using demineralised water and brushes. Grout of white cement under pressure was inserted into the holes, and on the surface area where a piece had been fractured. The two pieces were welded and fixed with a strap. Grout of white cement was again pressed into the holes, in order to hold the two ribbed titanium bars, with a diameter of 8 mm and length 25 cm, aiming at the support of the welding on the helix. At the end, the excess mortar was cleaned with a spatula, sponges and water and the process was completed (Fig. 15). Welding with mortar of same of constitution was also done at an area of the column where the section that was welded was found in place but needed support.

Fig. 15. Completion of intervention.

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[8]The constitution of mortar that was used for the sealing of cracks is: 2 parts white cement and 1 part marble powder.

[9]Mortar composition: 25% white cement, 25% quartz sand, 50% marble powder. A resin for cohesion of mortar, with the commercial name "REVINEX", was also added to the mix.

7.5. Completion of missing parts.

The anthemion on the eastern aspect presented loss of material at the top, which was most likely owed to the oxidation and expansion of the iron contact. The corroded metal element was removed, whereas two more holes were opened. In the central hole, a ribbed titanium bar of 6 mm diameter was inserted; the other two holes were filled with a non ribbed titanium bar in the form of a petal, of 3 mm diameter (Fig. 16). The titanium bars were fixed with white cement, which was pressed into the holes as grout before their insertion. At the end, the completion of the anthemion was done with mortar of the same constitution.

Fig. 16. Ribbed titanium bars and bar in petal shape, fixed with mortar.

7.6. Intervention for cohesion and strain resistance.

The following work was executed at the area of the cloak, aiming at the prevention of detachment of parts of material and as a treatment for strain resistance: Initially a hole was opened with a rotary drill and grout of white cement was inserted with a cartridge, so as to hold in place the ribbed titanium bar of a diameter 6 mm. Moreover, two holes were opened, in which grout was imported and then the double titanium bar of a diameter of 6 mm was placed. This bar was given a Π shape (Fig. 19). In addition, two holes were opened in the south-western helix and grout of white cement under pressure was inserted, so that the ribbed titanium bar would be held in place. The bar had a diameter of 6mm and a length of 20 cm. Finally, the excess mortar was cleaned with a spatula, sponges and demineralised water.

Fig. 19. Test placement of titanic contact in Π form.

7.7. Aesthetic restoration - retouchment.

Chromatic restoration was performed in the area of the column capital; the colours used were blue and red plastic colours and leaves of 22 carats gold (Fig. 20). The marble had previously been primed with the emulsion of acrylic resin "Mixion". The leaves of gold were placed approximately half an hour after the application of resin and the process was completed.

Fig. 20. Completion of aesthetic restoration.

RESULTS - CONCLUSIONS

The building of the Athens Academy and particularly the sculpture of Athena is a symbol of intellectual life since it was created. Today the palace of the Academy adorns one from the busiest areas of the Greek capital. It had been included in the Regional Attica Operational Program 2000-2006 for the implementation of the building's repair and the restoration of the sculptural and pictorial decoration. However, the corrosion factors in the city centre are acting aggressively on the manufacture materials of the building and the statues. Atmospheric pollution, frequent phenomena of vandalism, vibrations caused by earthquakes, executed work, vehicles, the subway, as well as the overpopulation of pigeons render the future of the monument uncertain. For these reasons, an extensive debate has taken place over the removal of the statues from the propylon and their replacement with copies, while the prototypes would be preserved in museum conditions. At present the authentic sculptures remain in their places, with the hope and belief that the conditions in our city will be improved soon, in order for the monuments to remain safe in their original places.

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CONSERVATION AND RESTORATION OF THE ARCHAEOLOGICAL SITE OF KOTZIA SQUARE, ATHENS - GREECE

V. LAMPROPOULOS, A. KARAMPOTSOS, A. TSORONI & P. TZANOULINOS

LAMPROPOULOS V.*, 64 - 66 Pandosias str., Athens 11142, Greece.
e-mail: blabro@teiath.gr
website: www.vlampropoulos.gr
KARAMPOTSOS A., 1 Politi str., Athens 11144, Greece.
e-mail: akarab@teiath.gr
TSORONI A., 9 Vergi str., Zografou 15772, Greece.
e-mail: atsoroni@yahoo.gr
TZANOULINOS P., 29 Pindou str, Argyroupoli 16451, Greece.
e-mail: praxis_tzanoulinos@yahoo.gr

*Author to whom correspondence should be addressed.

Εισαγωγή.

Οι εργασίες συντήρησης και ανάδειξης αφορούν σε αρχαιότητες που βρέθηκαν στις ανασκαφές της Πλατείας Κοτζιά και περιλαμβάνουν την Αχαρνική οδό, πηγάδια, ταφικό περίβολο και σαρκοφάγους, αγωγούς από λίθους, κονίαμα, κεραμικούς αγωγούς (πιόσχημους) και κεραμικούς κλιβάνους. Κατ' αρχήν τονίζουμε ότι οι εργασίες πραγματοποιήθηκαν με σύγχρονο τεχνικό εξοπλισμό για εφαρμογές μεθόδων συντήρησης και αποκατάστασης δομικών στοιχείων αρχαίων κατασκευών με τεκμηριωμένη και επιστημονικά αποδεκτή χρήση ειδικών υλικών και τεχνικών μέσων και μεθόδων που χρησιμοποιούνται γενικά στις εργασίες αναστήλωσης, ανάδειξης και αποκατάστασης μνημείων και ειδικότερα στις επεμβάσεις επί αρχαιοτήτων (αποκόλληση, μεταφορά, επανακατασκευή) και αρχαιολογικών χώρων, σύμφωνα με τους διεθνείς κανονισμούς και χάρτες που ισχύουν σε παρόμοια έργα. Το έργο το οποίο πραγματοποιήθηκε περιλαμβάνει επίσης κατασκευή αντίγραφων της επιφάνειας των παρειών της ανασκαφής, από ειδικό κονίαμα και χρωστικές, για αισθητική αποκατάσταση του ανασκαφικού χώρου.

Introduction.

The conservation and restoration works relate to the antiquities found during the excavations at Kotzia Square in Athens. They comprise the Acharnian Way, wells, a burial precinct with carnivorowses, pipelines of stone or mortar, ceramic pipelines and ceramic kilns. It is worth noticing that all the works were conducted with the use of the latest technical equipment regarding the application of conservation and restoration methods to the building elements of ancient constructions. All the international regulations and codes of practice regarding interventions on antiquities and archaeological sites (detachment, transportation, reconstruction), were followed meticulously. Both the use of specialist materials, and the current technological applications and equipment, were scientifically substantiated and accepted by the international community in similar conservation endeavors. The finished work also includes the aesthetic restoration of the excavation area, with the creation of copies of the surface of the adjacent area. These copies consist of special mortar and pigments.

Conservation Methods.

The conservation interventions on archaeological finds are divided in structural material analysis, cleaning, surface consolidation, and fortification. It is needless to say that every intervention does not necessarily include all the above-mentioned procedures. Nor is there one type of intervention applicable to all cases. Extended research is required in order for a conserver to opt for a particular methodology and the appropriate materials. The material and structure of the ancient object, the factors that affect its wear, the extent of its deterioration and the environment in which it is exposed, are all major contributing factors to the methodology and materials used. What is more, the technique in the use of any particular conservation material is of paramount importance, as the final outcome ought to meet the highest qualitative and aesthetic standards.

Specifications of the conservation methods for archaeological findings.

What follows is the conservation and restoration process for archaeological findings, together with their respective specifications, according to the extent of their wear:

1. The analyses of the structural material of the depositions (ceramic, stone and mortar) were conducted with the use of especially prototyped chemical (compleximetry, gravimetric methods etc.) and physicochemical techniques.

The generated analyses serve a dual purpose. Firstly, they relate vital information on both ancient technologies, and the effect of the environment on the structural material of archaeological findings. Secondly, the analyses formed the foundation on which the restoration interventions were based. These included the cleaning, the fortification, the filling in, and the aesthetical restoration of ceramics, stone and mortar; the determination of the composition of the mortar, which was used in order to imitate the original schist stone; and the process of joining together and consolidating the entire project.

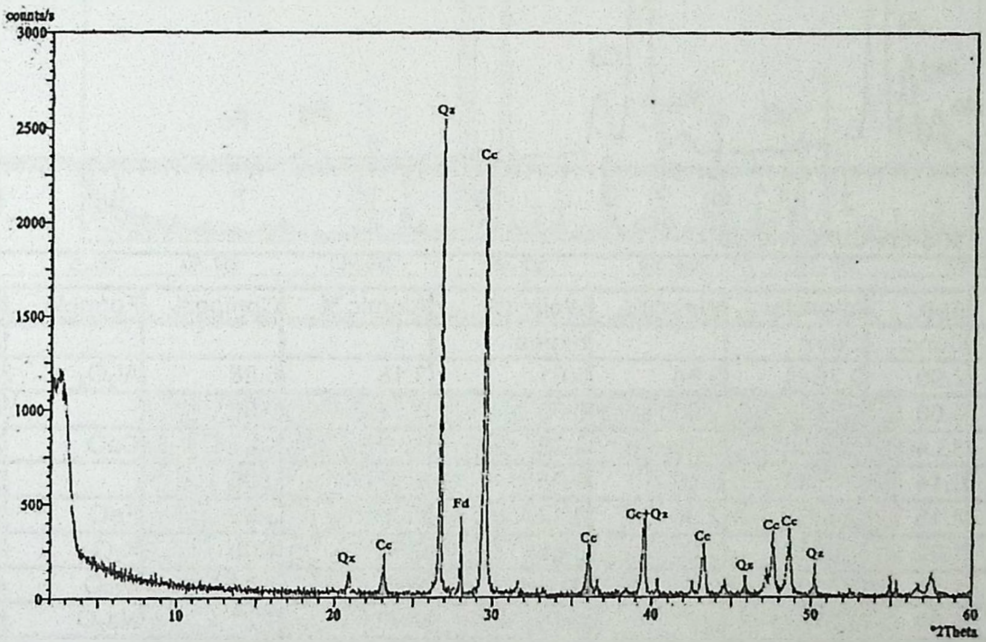
2. The depositions of a variety of substances were removed by using the appropriate "painless" cleaning methods for ceramics, stone and mortar, which comprise the employment of distilled water and specialist compatible cleaning pulps. pH measurements were taken at the end of each cleaning phase, together with measurements of the electric conductibility of the solutions, in order to determine the total removal of both acid of alkaline residues from the cleaning, and of soluble salts.

Soluble salts were also removed from the surface and the pores of the ancient objects with the aid of pulps soaked in distilled water. Measurements of the electric conductibility of the objects were then taken in order to confirm the completion of the cleaning process.

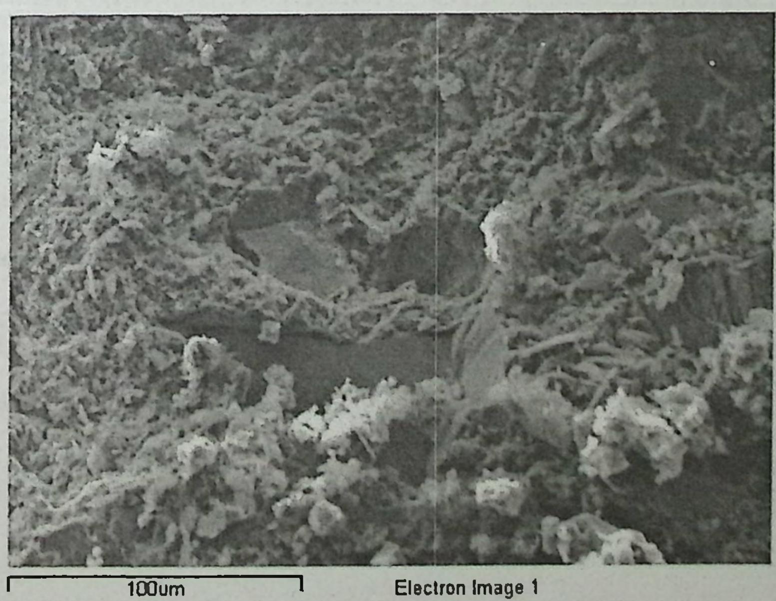
Every adopted cleaning method had previously been tested on a tiny surface of the object, so that the most appropriate should be chosen. The appropriate method is one which does not "injure" the object, and cleans effectively without causing distress to the "noble patina" on the surface of the object.

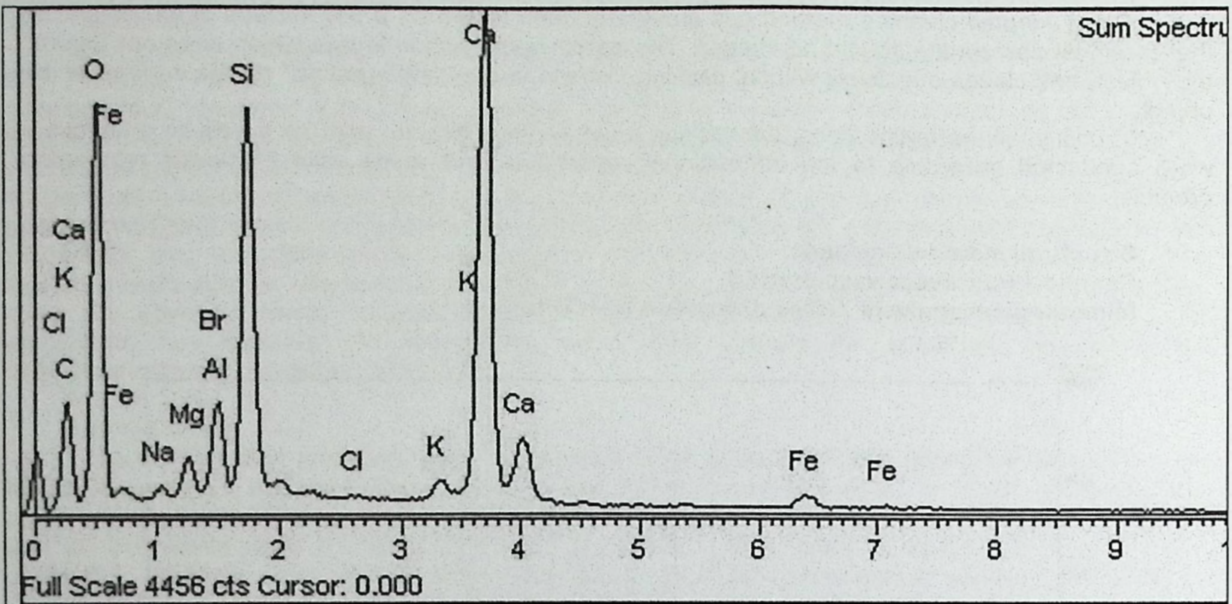
3. Lastly, all the fortifications, the sticking together, the filling in, and the aesthetic restoration, were conducted according to the international regulations and maps valid in similar restoration projects.

Structural material analyses.
Sample 1 (carnivorowses mortar).
Mineralogical analysis X-rays diffraction (X-R.D.).



Elementary analysis of scanning electron microscopy (S.E.M. - E.D.X.A.) x5000.





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Al K	2.90	0.7544	3.64	0.61	3.18	6.88	Al_2O_3	0.44
Br L	0.00	0.7030	0.00	0.00	0.00	0.00		0.00
Ca K	33.40	0.9897	32.00	0.32	18.79	44.78	CaO	2.59
Cl K	0.14	0.7537	0.18	0.05	0.12	0.00		0.02
Fe K	2.15	0.8136	2.50	0.14	1.06	3.22	FeO	0.15
K K	1.02	1.0798	0.90	0.06	0.54	1.08	K_2O	0.07
Mg K	1.54	0.6539	2.24	0.09	2.17	3.71	MgO	0.30
Na K	0.69	0.6764	0.97	0.10	0.99	1.31	Na_2O	0.14
Si K	15.68	0.8188	18.16	0.20	15.21	38.84	SiO_2	2.10
O			39.41	0.47	57.96			7.98
Totals			100.00					
							Cation sum	5.78

Observations.

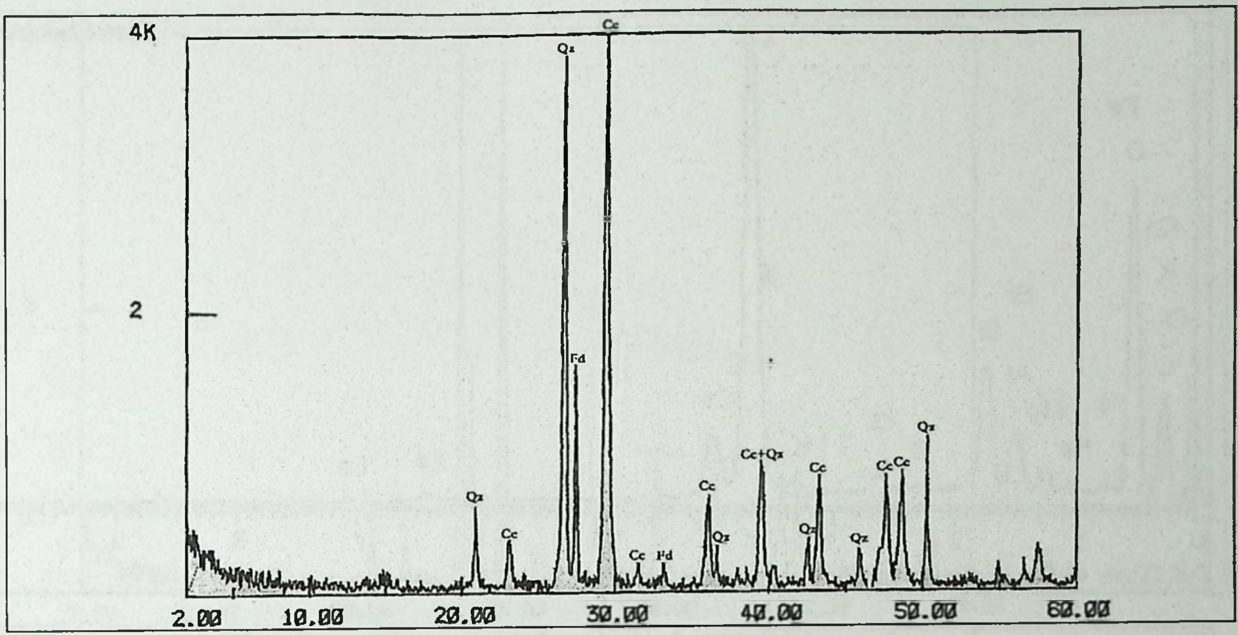
1. The mineralogical analysis of the sample demonstrates occurrence of limestone, quartz and aluminosilicate minerals.
2. The elementary analysis demonstrates occurrence of Ca, Mg, Si, Al, Fe and other elements in small concentrations.
3. The microscopic analysis illustrates that the mortar has grains of a relatively small diameter, while the aggregates consist of medium-size grains.
4. The measurement of the porosity demonstrates that the sample has 17% porosity.
5. The measurement of the special weight of the sample shows a special weight of 2,9 gr^{*}/cm^3.

Conclusion.

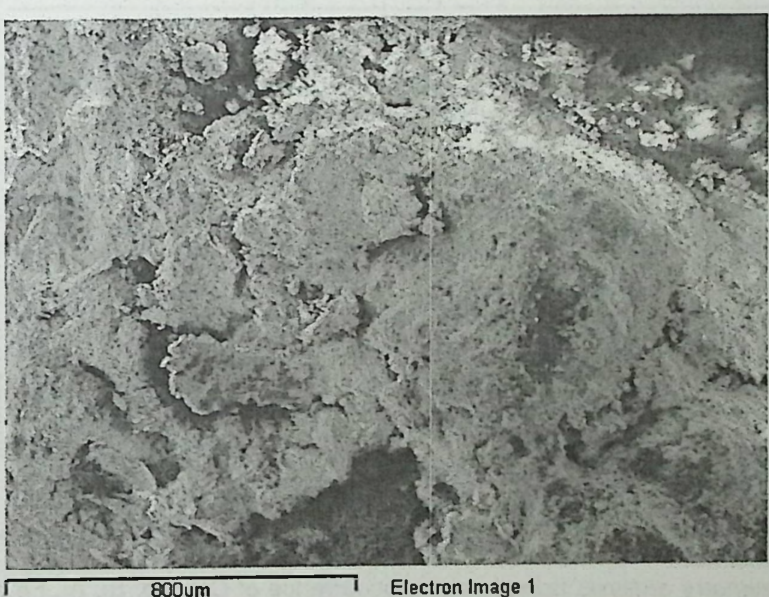
The sample is made of mortar consisting of lime, sand of quartz and pozzolanic earth.

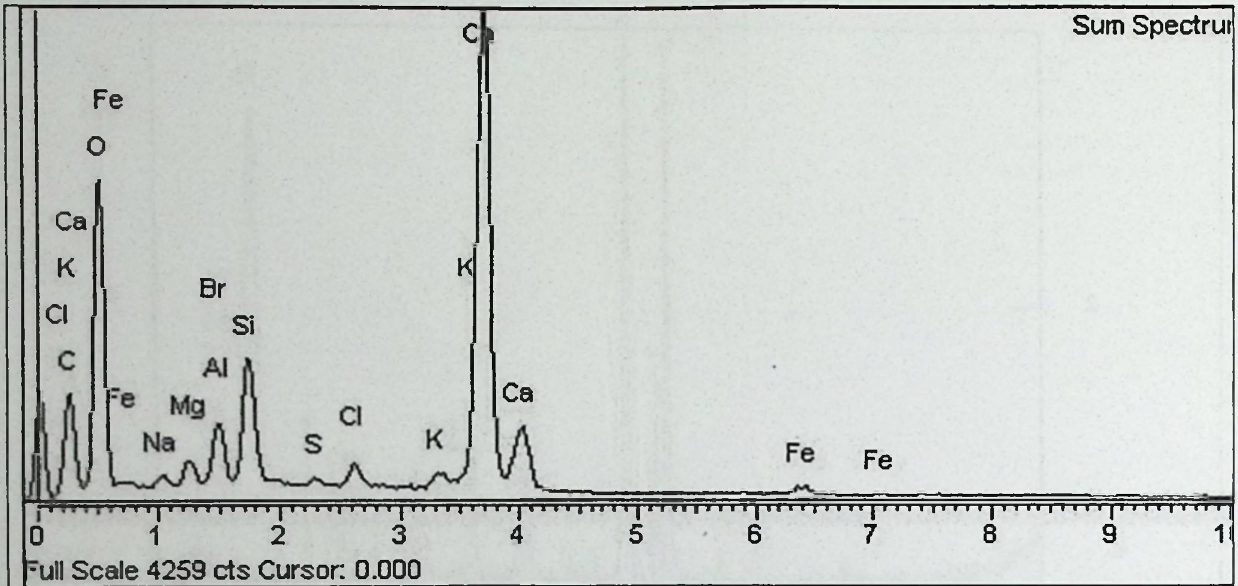
Sample 2 (carnivorowses mortar).

Mineralogical analysis X-rays diffraction (X-R.D.).



Elementary analysis of scanning electron microscopy (S.E.M. - E.D.X.A.) x750.





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Al K	1.64	0.7423	2.39	0.70	2.29	4.51	Al_2O_3	0.33
Br L	2.33	0.6924	3.64	1.39	1.18	0.00		0.17
Ca K	41.43	1.0140	44.12	0.81	28.49	61.73	CaO	4.10
Cl K	1.11	0.7956	1.51	0.08	1.10	0.00		0.16
Fe K	1.42	0.8156	1.87	0.17	0.87	2.41	FeO	0.13
K K	0.93	1.1303	0.89	0.08	0.59	1.07	K_2O	0.08
Mg K	1.19	0.6363	2.02	0.11	2.16	3.36	MgO	0.31
Na K	0.84	0.6596	1.37	0.14	1.55	1.85	Na_2O	0.22
S K	0.38	0.8624	0.47	0.07	0.38	1.18	SO_3	0.05
Si K	6.34	0.7818	8.76	0.20	8.08	18.75	SiO_2	1.16
O			32.95	0.73	53.32			7.67
Totals			100.00					
							Cation sum	6.39

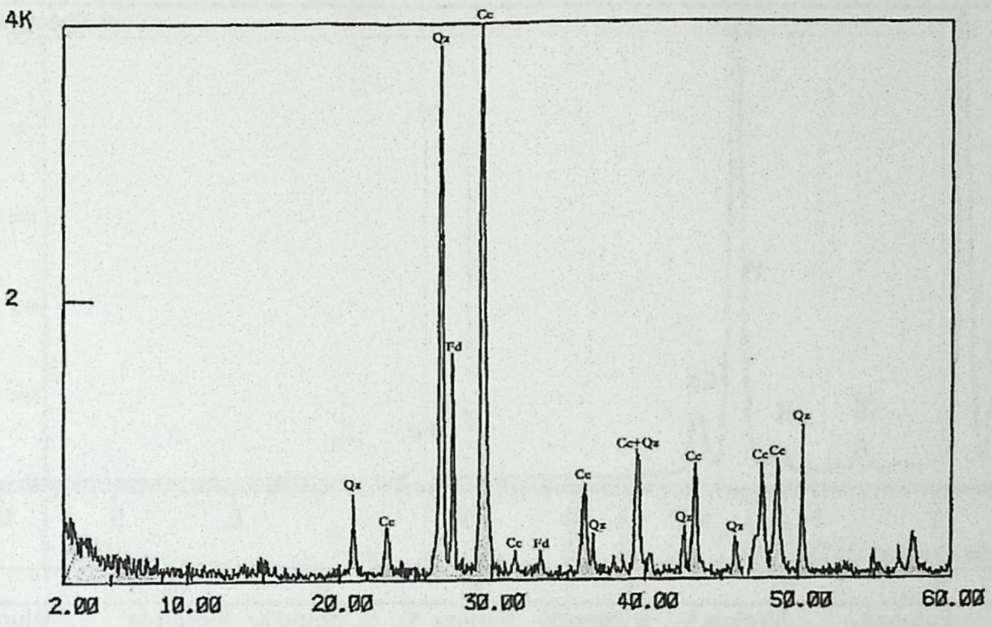
Observations.

1. The mineralogical analysis of the sample demonstrates occurrence of limestone, quartz and aluminosilicate minerals.
2. The elementary analysis demonstrates occurrence of Ca, Mg, Si, Al, Fe and other elements in small concentrations.
3. The microscopic analysis illustrates that the mortar has grains of a relatively small diameter, while the aggregates consist of large-size grains.
4. The measurement of the porosity demonstrates that the sample has 19% porosity.
5. The measurement of the special weight of the sample shows a special weight of 3,1 gr/cm^3.

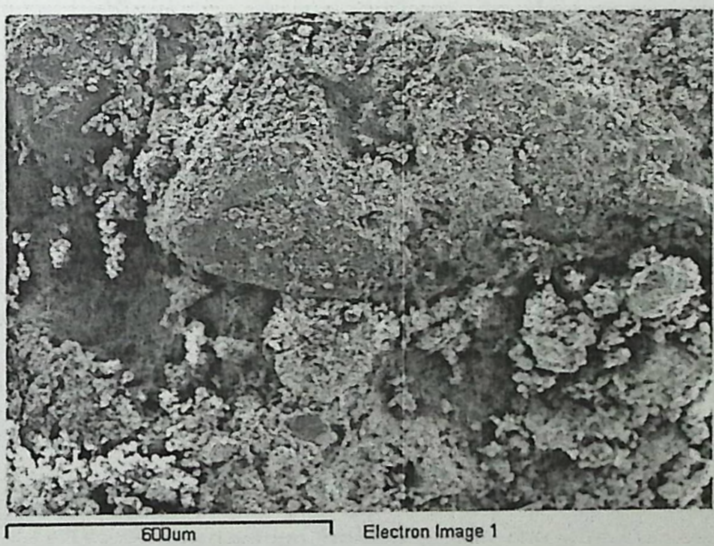
Conclusion.

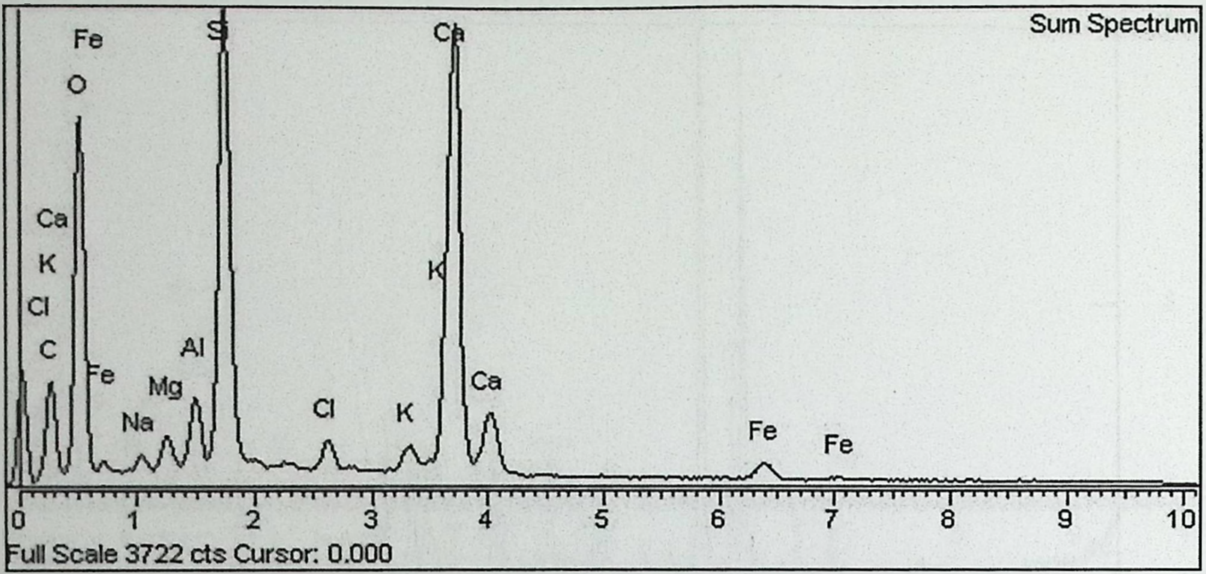
The sample is made of mortar consisting of lime, sand of quartz and pozzolanic earth.

Sample 3 (stone masonry mortar).
Mineralogical analysis X-rays diffraction (X-R.D.).



Elementary analysis of scanning electron microscopy (S.E.M. - E.D.X.A.) x1000.





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Al K	2.53	0.7624	3.00	0.08	2.60	5.67	Al_2O_3	0.35
Ca K	31.01	0.9784	28.60	0.17	16.68	40.01	CaO	2.26
Cl K	1.34	0.7461	1.63	0.07	1.07	0.00		0.15
Fe K	2.45	0.8154	2.71	0.15	1.13	3.48	FeO	0.15
K K	1.26	1.0576	1.08	0.07	0.64	1.30	K_2O	0.09
Mg K	1.42	0.6585	1.95	0.08	1.87	3.23	MgO	0.25
Na K	0.93	0.6860	1.22	0.10	1.24	1.65	Na_2O	0.17
Si K	18.56	0.8321	20.12	0.13	16.75	43.04	SiO_2	2.27
O			39.71	0.19	58.01			7.85
Totals			100.00					
							Cation sum	5.54

Observations.

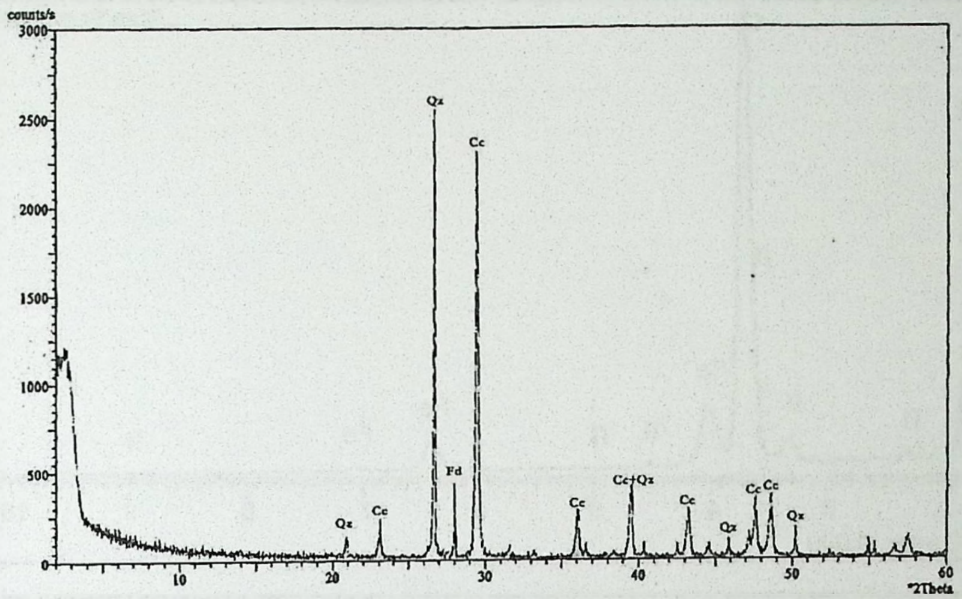
1. The mineralogical analysis of the sample demonstrates occurrence of limestone, quartz and aluminosilicate minerals.
2. The elementary analysis demonstrates occurrence of Ca, Mg, Si, Al, Fe and other elements in small concentrations.
3. The microscopic analysis illustrates that the mortar has grains of a relatively small diameter, and the aggregates consist of small-size grains.
4. The measurement of the porosity demonstrates that the sample has 15% porosity.
5. The measurement of the special weight of the sample shows a special weight of 3,3 gr/cm^3.

Conclusion.

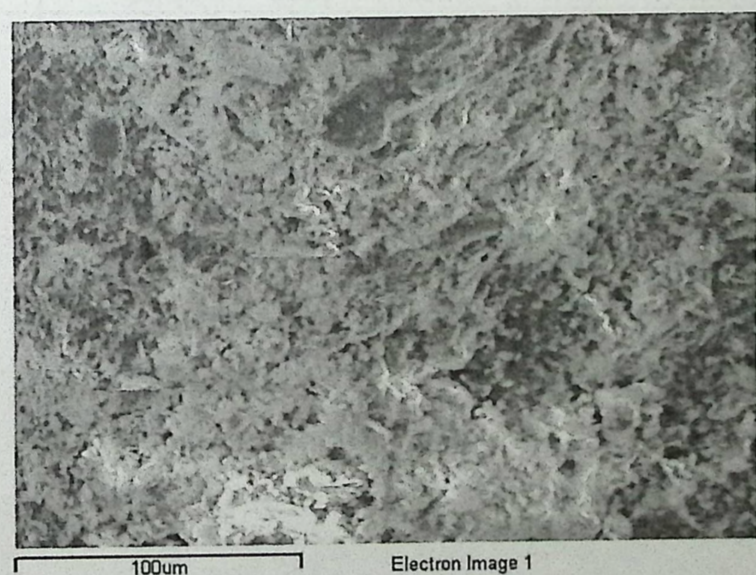
The sample is made of mortar consisting of lime, sand of quartz and pozzolanic earth.

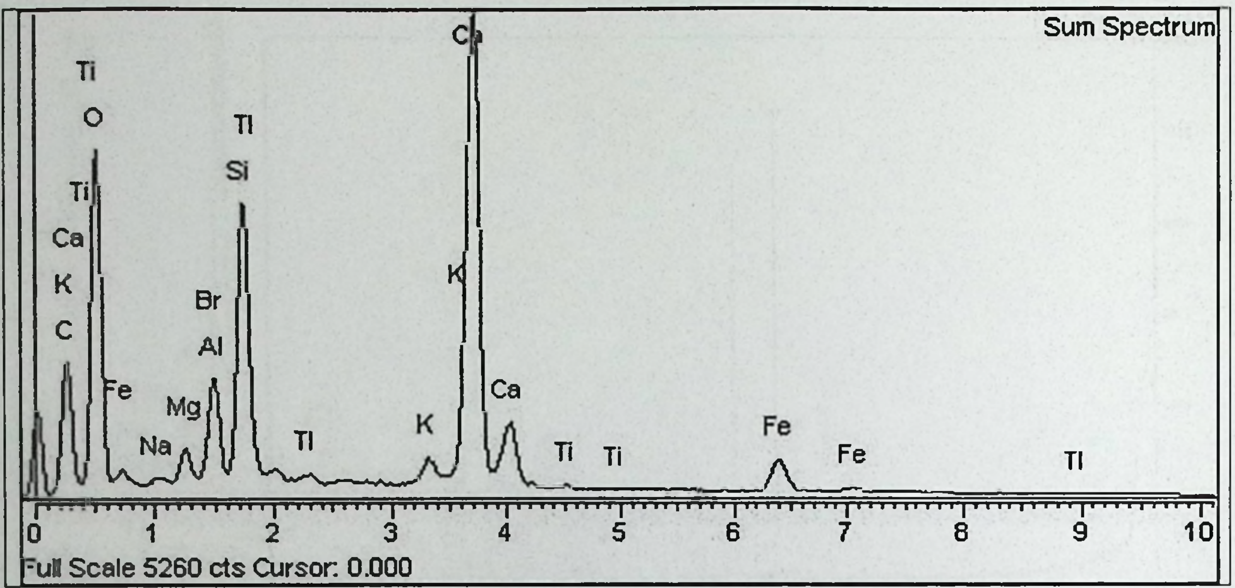
Sample 4 (stone masonry mortar).

Mineralogical analysis X-rays diffraction (X-R.D.).



Elementary analysis of scanning electron microscopy (S.E.M. - E.D.X.A.) x5000.





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Al K	2.25	0.7443	2.80	0.55	2.65	5.30	Al_2O_3	0.37
Br L	3.29	0.6941	4.41	1.09	1.41	0.00		0.20
Ca K	34.02	0.9956	31.75	0.47	20.19	44.42	CaO	2.81
Fe K	5.30	0.8295	5.94	0.18	2.71	7.64	FeO	0.38
K K	1.34	1.0783	1.16	0.06	0.75	1.39	K_2O	0.10
Mg K	1.35	0.6385	1.96	0.08	2.05	3.25	MgO	0.29
Na K	0.53	0.6562	0.76	0.09	0.84	1.02	Na_2O	0.12
Si K	11.79	0.7682	14.26	0.23	12.94	30.51	SiO_2	1.80
Ti K	0.31	0.7557	0.38	0.07	0.20	0.63	TiO_2	0.03
Tl M	1.06	0.7127	1.38	0.15	0.17	1.43	Tl_2O	0.02
O			35.21	0.59	56.09			7.80
Totals			100.00					
							Cation sum	5.91

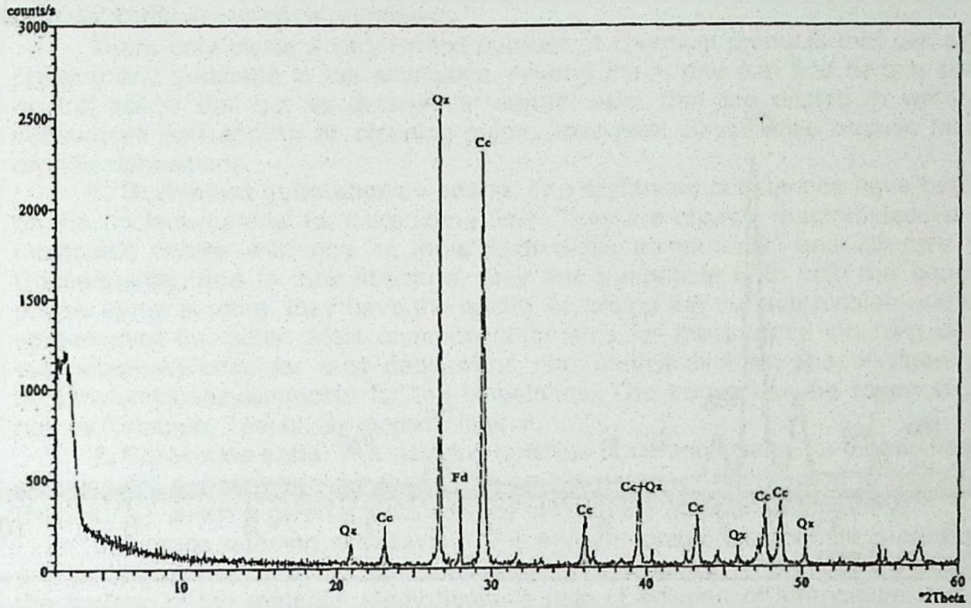
Observations.

1. The mineralogical analysis of the sample demonstrates occurrence of limestone, quartz and aluminosilicate minerals.
2. The elementary analysis demonstrates occurrence of Ca, Mg, Si, Al, Fe and other elements in small concentrations.
3. The microscopic analysis illustrates that the mortar has grains of a relatively small diameter, and the aggregates consist of small-size grains.
4. The measurement of the porosity demonstrates that the sample has 15% porosity.
5. The measurement of the special weight of the sample shows a special weight of 3,2 gr/cm^3.

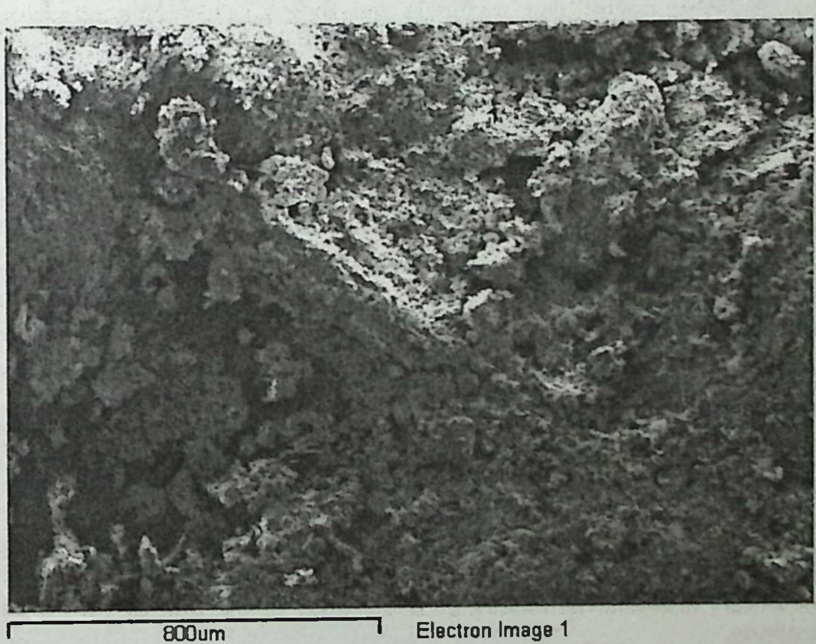
Conclusion.

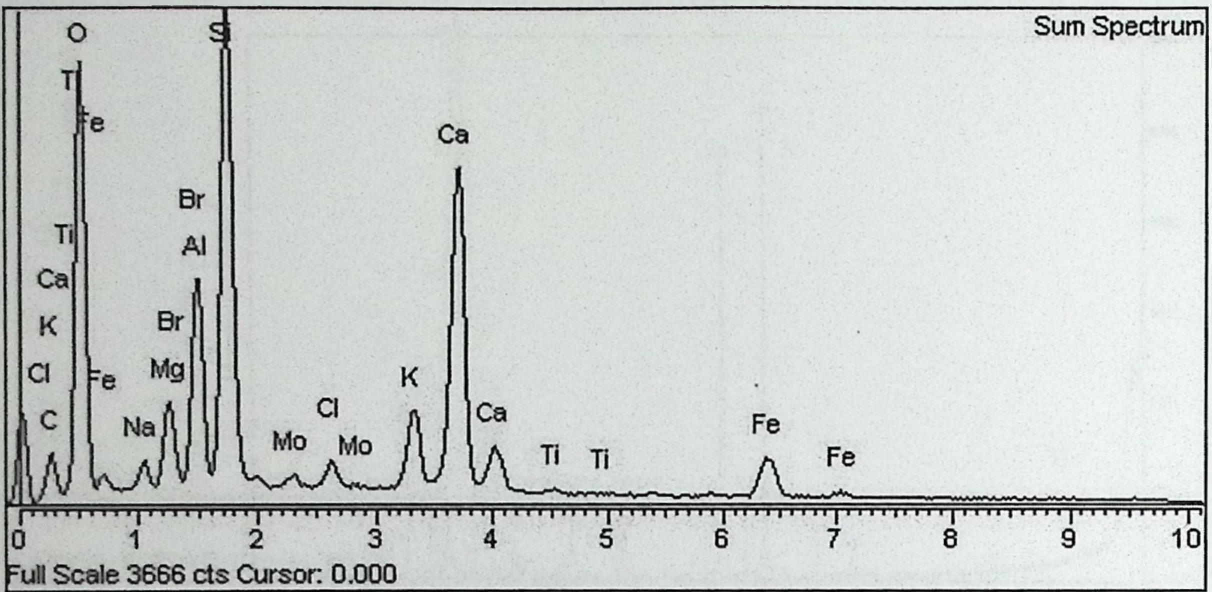
The sample is made of mortar consisting of lime, sand of quartz and pozzolanic earth.

Sample 5 (stone masonry mortar).
Mineralogical analysis X-rays diffraction (X-R.D.).



Elementary analysis of scanning electron microscopy (S.E.M. - E.D.X.A.) x750.





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Al K	5.24	0.7545	5.35	0.61	4.72	10.11	Al_2O_3	0.63
Br L	3.68	0.7033	4.02	1.23	1.20	0.00		0.16
Ca K	20.44	0.9533	16.50	0.29	9.81	23.09	CaO	1.32
Cl K	1.04	0.7113	1.13	0.06	0.76	0.00		0.10
Fe K	5.66	0.8336	5.23	0.17	2.23	6.72	FeO	0.30
K K	4.64	1.0155	3.52	0.09	2.14	4.23	K_2O	0.29
Mg K	3.17	0.6752	3.62	0.10	3.55	6.00	MgO	0.48
Mo L	1.13	0.6690	1.30	0.13	0.32	1.95	MoO_3	0.04
Na K	1.41	0.7133	1.52	0.09	1.57	2.04	Na_2O	0.21
Si K	18.20	0.7491	18.71	0.32	15.87	40.02	SiO_2	2.13
Ti K	0.41	0.7779	0.41	0.06	0.20	0.68	TiO_2	0.03
O			38.70	0.69	57.63			7.74
Totals			100.00					
							Cation sum	5.43

Observations.

1. The mineralogical analysis of the sample demonstrates occurrence of limestone, quartz and aluminosilicate minerals.
2. The elementary analysis demonstrates occurrence of Ca, Mg, Si, Al, Fe and other elements in small concentrations.
3. The microscopic analysis illustrates that the mortar has grains of a relatively small diameter, and the aggregates consist of small-size grains.
4. The measurement of the porosity demonstrates that the sample has 15% porosity.
5. The measurement of the special weight of the sample shows a special weight of 3,5 gr^{*}/cm^3.

Conclusion.

The sample is made of mortar consisting of lime, sand of quartz and pozzolanic earth.

Cleaning.

Mechanical cleaning methods.

Use of a range of hand tools, such as scalpels, chisels, needles and low revolution electric drills.

Chemical cleaning methods.

There only exists a very limited number of chemical products that can safely be used without causing any problems to the antiquities. Among them, one can find certain surfactant substances - neutral soaps that act as detergents; certain salts that are diluted in water, mixed with neutral substances and applied as cleaning pulps; absorbent clays; while organic solvents are applied on organic depositions.

1. Surfactant substances - soaps. The surfactant substances have been used as detergents on the ancient material for quite some time. They are organic macromolecules consisting of carbon molecules chains with one or more hydrophilic compounds, and strongly polar at either end. Consequently, due to their structure, they are compatible both with the aqueous and the organic phase. What is more, they have the quality of raising the surface tension and of making one phase spread over the other. Most common detergents for the surface cleaning of the material are the exametaphosphates for dust depositions, the methylcellulose, the alkylbenzylsulphonics and the dimethylamylbenzylammonia for the limestones. The above can be found in commerce under the names Texapon, Teepol, Synperonic N et al.

2. Carbonate salts. The cleaning qualities of carbonic salts have been known for a long time. In cleaning for conservation purposes, the only substance widely used is the ammonium bicarbonate (NH_4HCO_3), which is given a more alkaline pH with the addition of ammonia.

In surface cleaning, a solution of 7% w/v ammonium bicarbonate is created by constant stirring and adding pieces of neutral paper carboxymethylcellulose. The produced pulp is applied directly on the surface of the material. Many times, a pulp of solution of ammonium carbonate ($(NH_4)_2CO_3$) is used instead of an ammonium bicarbonate pulp. The latter creates a slightly alkaline environment that favors the removal of soluble salts which are found in depositions.

3. Pulps for direct application on the material surface. Commonly used substances in pulps are the carbonate salts of ammonium and sodium (NH_4HCO_3 - $NaHCO_3$) and the ethylendiamintetraacetic acid (E.D.T.A.) or the disodium salt, which is more easily soluble than E.D.T.A.. Substances, such as methylcellulose or carboxymethylcellulose, small pieces of neutral paper and absorbent clays, are added to the mix for the creation of the pulp.

The pulp is mechanically removed from the surface, usually with a spatula. The surface is then cleaned with distilled water and a brush, in order to dispose of the remaining pulp and corrosion substances, such as soluble salts that have been dissolved or formed. In many occasions, when the surface is crumbling, a dry absorbent sheet of neutral paper or Japanese paper is used under the pulp. In this way, the crumbling surface does not get distressed and the pulp can be easily removed without leaving any residue on the surface. An additional benefit of a pulp is that it can be used on vertical surfaces.

The composition of a cleaning pulp varies according to the situation it is used in.

a. Mora pulp: H_2O: 100 cc, NH_4HCO_3 and $NaHCO_3$: 6 gr, E.D.T.A.: 2,5 gr, Desogen:1 gr and carboxymethylcallulose or neutral paper: 6 gr.

b. E.D.T.A. pulps: H_2O: 100 cc, E.D.T.A.: 3 gr, $NaHCO_3$: 4 gr, NH_4HCO_3: 5 gr, and carboxymethylcallulose or neutral paper: 10 gr.

c. AB57 pulp: H_2O: 100 cc, NH_4HCO_3: 3 gr, $NaHCO_3$: 5 gr, E.D.T.A.: 2,5 gr, Desogen:1 cc and carboxymethylcallulose or neutral paper: 6 gr.

The quantity of E.D.T.A. varies and in some cases it can reach 10 - 12,5 gr. Ammonia (NH_3) and triethanolamine ($(C_2H_4OH_3)N$) are also usually added in order to facilitate the dissolution of oxidized fatty substances that may have formed on the crust. The use of sodium bicarbonate ($NaHCO_3$) is sometimes avoided as it produces soluble sodium salts which are corrosive to the surface.

Desogen is a surfactant substance and a salt of quaternal ammonium; its advantage lies on the fact that it lowers the surfactant tension between the crust and the solution during cleaning, which eases the removal of the solution. It definitely has to be completely colorless in order to prevent staining of the material.

4. Organic solvents. Organic solvents are primarily used for the removal of colors and fatty substances that have either created stains on the surface, or have saturated the pores of the material. Ethanol, aceton, white spirit, 1,1,1-trichloroethan et al, are customarily used.

5. Use of absorbent clays. Both argils used in this process, sepiolite and attapulgite, are aluminosilicate minerals of magnesium. Both of them have roughly the same chemical composition and mineralogical structure. More specifically, they are both hydrated magnesium silicates with a double chain of silicon and oxygen in tetrahedra, which are joined in parallel direction with the length axis of the crystal.

Their most significant quality is their great specific surface, about 130 m^2/gr, that is highly electrically charged, which allows them to absorb large quantities of water or other liquids.

disproportionately to their weight. For example, 1 Kgr attapulgite can absorb 1,5 Kgr of water and still occupy the same volume as it did on its dry state, as the water fills the empty spaces on the structure of the clay.

6. Use of organic pulps. This method has been invented and developed in order to achieve and accelerate the cleaning of surfaces that are sensitive or corroded due to their exposure to the open air. These surfaces are in danger of being damaged, should water sprayings or other more unsafe methods be used. The method involves the application of a thixotropic pulp, containing an adequate quantity of sepiolite or attapulgite, on the surface of the material. A solution containing the following elements is produced:

a. 1 lt water.

b. 50 gr urea ($(NH_2)_2CO$).

c. 20 ml glycerine ($(CH_2OH)_2CHOH$).

The required quantity of sepiolite or attapulgite is then added to the solution, so that a thixotropic pulp is produced. The pulp needs to have a thickness of at least 2 cm and to be covered by a sheet of polyethylen, which should be well adhered to and stuck together at the edges, so that the water in the pulp does not vapor.

Removal of organic depositions.

Organic depositions, such as moss, algae, lichens etc., customarily grow on surfaces that are exposed to a particularly humid and shady environment, are northward looking, or tend to gather still water for a number of reasons. The microorganisms perform chemical and mechanical actions on the material which cause disruption on the surface, different types of corrosion, or create color stains. Some kinds of algae and bacteria bring the iron from the interior of the material out on its surface, where it gets oxidized. The stains caused by this oxidization are not easily removed. What is more, the lichens, which cohabite with the algae and the fungi, penetrate the small cracks thus performing mechanical pressure on the walls of the crack. Additionally, they infuse both the surface and the interior of the pores with corrosive solutions of carbonic and oxalate acid for the alkalic materials. However, in some cases the lichens form calcium oxalate and therefore act as stabilizers. In these cases, the lichens should not be removed.

Certain chemical products that aim at fighting the cyanoalgae and chloroalgae algae are compounds of quaternal ammonium, like hyamin by Rohm and Haas, combined with absorbent clays, such as attapulgite. One such biocide is Desogen, which is produced by Ciba Geigy. The advantages of such a combination are its stability and the fact that it remains active for a long period of time. Other biocides with satisfactory results against the algae are compounds of copper with ammonia and complexes of copper with hydrazine. Satisfactory results against moss, algae and lichens, have been obtained from aqueous solution 1 - 2 % lithium hypochloride and biocides with neutral pH, such as biocides Lito 7 and Lito 3, which are produced by Ciba Geigy.

Substances used on algae have been suggested and used for the removal of lichens. These are borate and organic compounds of tin and quaternal amins in combination with specific absorbent clays, namely sepiolite or attapulgite.

In order to remove fungi, an antibiogram needs to be performed, so that the right antibiotics can be prescribed. The most commonly used biocides are abicilline, the semidazolinylurea and the bezalconium chloride.

The most effective, and therefore the most commonly used biocides available in the trade, are: Desogen, which acts mainly on bacteria, chloroalgae and fungi; Primatol M50 by Ciba Geigy; Primatol 3588 by Ciba Geigy; Vancide 51 by R.T. Vanderbilt Co. Inc. - U.S.A. et al.

Finally, it should be noted that hydrogen peroxide solution (H_2O_2) 10 - 30% w/v (perhydrol) is normally used in the cleaning of organic depositions. This is because it demonstrates intensely oxidizing qualities that dissolve/break down organic matter, while acting as a whitener on stains created by lichens. The effectiveness of perhydrol is limited in cases where the material contains admixtures with oxides of Fe^{2+} (FeO), as these get oxidized and produce oxides of Fe^{3+}, thus giving the material a red hue in the cleaning area.

Removal of soluble salts from the surface and the pores of the material.

As already stated, the soluble salts that are found on the surface and in the pores of the material constitute major corrosive factors. Therefore, they should be removed as meticulously as possible. Water is collected after changing each pulp. The specific electric conductivity of this water is calculated and the leaching stops when the conductivity is stabilized in low numbers. The material is then let to dry.

The specific electric conductibility C of a solution is measured in mhos or siemens, and can be expressed by the following formula:

C=1/R

where R is the electric resistance of the solution, which is measured in ohms.

The conductibility of a solution that is measured in 25 °C by using two platinum electrodes each with a surface of 1 cm^2 and a distance between them of 1 cm, is called specific electric conductivity. Therefore, the specific electric conductibility, which is measured by a conductivity meter, is calculated in mhos/cm^2 or siemens/cm^2. For example, the specific electric conductibility of distilled water is 5 μmhos/cm^2, or approximately 5.10^{-6} mhos/cm^2 .

The removal of the soluble salts from the pores and the surface of the material is checked by measuring the water conductivity. A pulp or a cellulose sheet is immersed in the water and then let to dry. It is then immersed in distilled water with a specific conductivity that has been measured and regulated not to exceed a few μS/cm^2. The pulp is left in the water for a length of time that allows the soluble salts that had been previously absorbed to get diluted. The specific conductivity of the water is then measured again. By measuring the specific conductivity of a series of pulps of the same weight, it is observed that the specific conductivity demonstrates a steep decline in the first few applications, while remaining relatively stable consequently. The application of pulps on the surface of the material discontinues when the conductivity gets stabilized at a low rate; and he material is then dried off.

The typical process is illustrated by the following diagram:

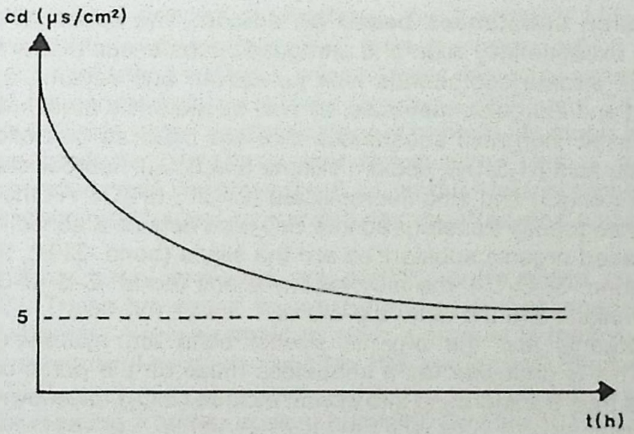


Diagram of specific conductivity-time, during removal of soluble salts from the surface of porous materials.

Material securing/consolidation.

The employed consolidation processes include low pressure sprayings of solidifying solutions; applications of solidifying solutions carried on special neutral paper pulps; and microenemas of solidifying solutions in the case of small cracks. In cases of extended corrosion and cracks on the surface of stone, ceramics and mortar, we intervened with enemas of the same composition as the original material; the composition of these enemas resulted from the tests and analyses previously mentioned. Special structural materials were employed in order to fight humidity, either environmental or rising. These materials were compatible and reversible; and caused the surface and pores to become hydrophobic. In other words, water in its liquid state was prevented from penetrating the structural material, while at the same time water in its gaseous state was allowed to evaporate from the material.

Consolidation process.

The effectiveness of a consolidation process depends on a large extent on the depth of penetration of the consolidation substance into the original material. A number of factors need to be regulated in order to achieve optimal results: the application method, the concentration of the substance, the type of diluter, the time of application, the pressure and the work temperature.

Same methods can be employed both on small objects that have been transferred to the laboratory, and larger objects that cannot be transported and need to be treated in situ. Such methods include applications of the consolidation material with a paintbrush until the original material cannot absorb any more; and spraying applications. The depth of penetration can be improved by progressively thickening the consolidating solution. However, both methods, and in particular the spraying method, cannot achieve satisfactory saturation results

A number of alternative consolidation methods are favored when objects can be transported to the lab, as they achieve better saturation results:

a. Full immersion of the object in the consolidating solution.

b. Soaking of the object in the consolidating material in vacuum.

During in situ consolidation, the material is initially strayed with the diluter used in the consolidating solution. The solvent, being a volatile and viscous liquid, deeply penetrates the material; this is followed by an application of the consolidating solution.

Consolidation substances.

These are the consolidation substances used when treating the material in this project:

1. Consolidation substances based on calcium hydroxide ($Ca(OH)_2$).

The agency of the environmental carbon dioxide on the calcium hydroxide results in the formation of calcium carbonate ($CaCO_3$), which has a consolidating effect on the surface and pores of the material:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

2. Consolidation substances based on silicon. The spectrum of consolidation substances containing silicon is exceptionally wide and comprises substances that are extremely different to each other. These include silicate compounds with potassium and sodium, as well as resins. They also include both organic and inorganic materials, as well as materials at an in-between state.

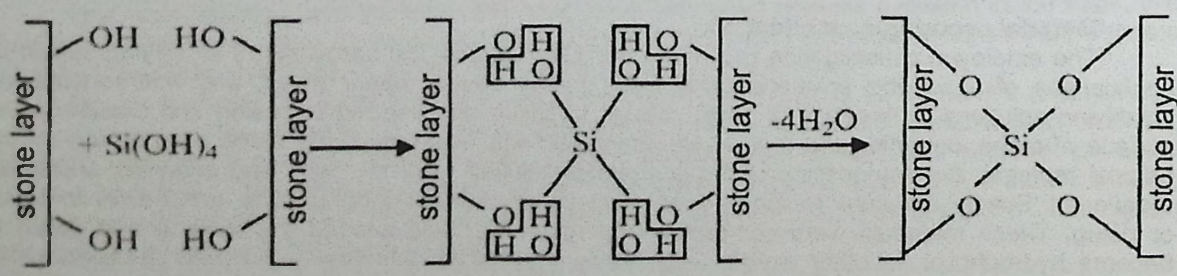
The silicon-based inorganic substances that are used as consolidators are orthosilicate acid (H_4SiO_4), metasilicate acid (H_2SiO_3), sodium silicate (Na_2SiO_3), fluorosilicate acid (H_2SiF_6), magnesium fluorosilicate ($MgSiF_6.6H_2O$) and zinc fluorosilicate ($ZnSiF_6.6H_2O$). All the above are transformed into H_4SiO_4, which is consequently transformed into SiO_2 and acts as a consolidating substance.

The silicon-based organic substances are the silans (bond -Si-H), the alkyl-silans (bond -Si-C-), the alcoxy-silans (bond -Si-O-C-), the alcyl-alcoxy-silans (bond -C-Si-O-C-), the silicons (bond -C-Si-O-), the poly-alcoxy-silans and the alcyl-aryl-silans.

Both the inorganic and the organic silicate salts are hydrolyzed with water thus forming orthosilicate acid. This is deposited as a shapeless mass on the pores of the stone, gradually losing the water it contains thus transforming into silicon dioxide (SiO_2), as shown in the following reaction:

$$Si(OH)_4 \rightarrow SiO_2\downarrow + 2H_2O$$

This creates electrostatic bonds that connect the polarized surfaces in the inside of the pores, as seen in the diagram:

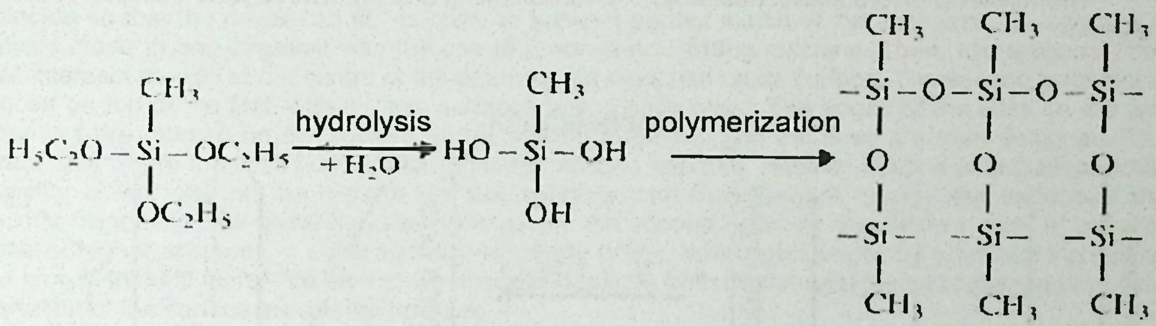


In the case of inorganic silicate salts, hydrolysis forms the respective hydroxide:

$$Na_2SiO_3 + 3H_2O \rightarrow H_4SiO_4\downarrow + 2NaOH$$

The hydroxides of alkalis favor the formation of soluble salts, e.g. sodium carbonate or sodium sulphate, which need to get immediately removed from the site in order to avoid damaging the stone material.

The alcyl-alcoxy-silans characterized that the bond -Si-C-O- hydrolyze easily and the product of this hydrolysis can polymerize, to give linear structures more or less branched, according to the reaction:

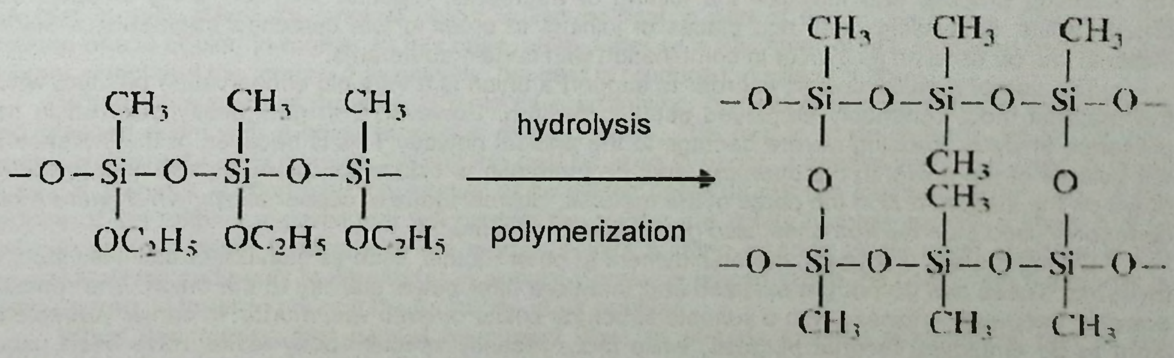


The most widely used consolidator with alkyl-alcoxysilans is Rhodorsil X54-802 by Rhone Poulenc. It has been used on marble and limestone materials in general, and has also produced satisfactory results on laboratory tests on samples. This particular product is a methyl-trimethoxy-silan with solvent 2-ethoxy-ethanol that can be easily hydrolyzed in the presence of a small quantity of water.

Another product in the same category is Brethane, by Colebrand Ltd, which is an alcylo-trimethoxy-silan. It has the advantage of remaining fluid for a few hours, which makes it possible to direct it for some time after the application thus achieving a larger degree of saturation. Other products in the same category used for consolidation are Dow Corning Z-6070 and T4-0149, both by Dow Chemical. Together with ethyl-silicate ester, another category of products found in the trade and used for consolidation comprises products containing alcyl-alcoxy-silan. This is because their alcylic compounds do not get hydrolyzed, and therefore the final product has hydrophobic qualities. Such commercial products are Rinforzante H, used for sandstones, by Wacker Chemie, and Tegovakon T by Th. Goldschmidt A.G..

Other products that have been employed are partially polymerized and contain a certain proportion of bonds -Si-O-C-. These are easier to get hydrolyzed and polymerized, which allows for better saturation of stone materials. A key example of such a product is methyl-ethoxy-polysiloxane. This category includes the commercial products Dri Film 104 by General Electric, and Tegosivin HL 100 by Th. Goldschmidt A.G.. Tegosivin is being portrayed by the manufacturers as a modified alcoxy-siloxan that is appropriate for creating a barrier against humidity. Dri Film 104 produces fortified silicon when being mixed with an acrylic resin; this gets polymerized in linear chains, without the formation of side bonds.

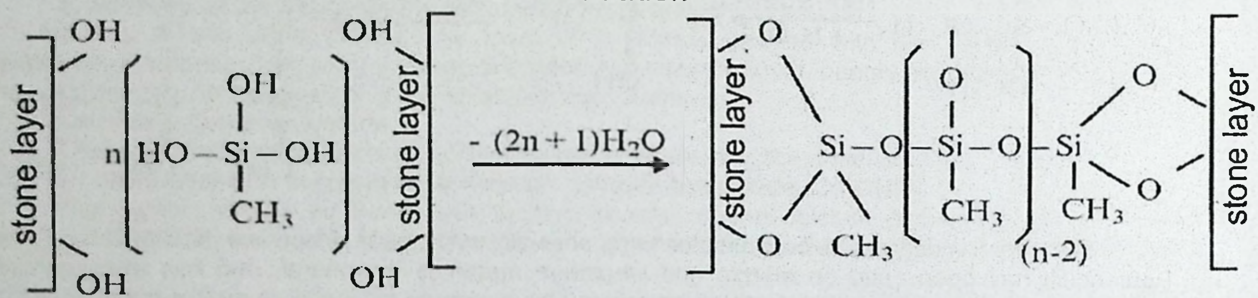
Lastly, consolidation can be achieved by making use of poly-siloxans, which are substances that have already been polymerized and can consequently create further chemical bonds. As a general rule, the qualities of theses polymers can be modified in accordance to the kind and the length of chain and the kind and the number of alkyls and aryls in the bonds with silicon.



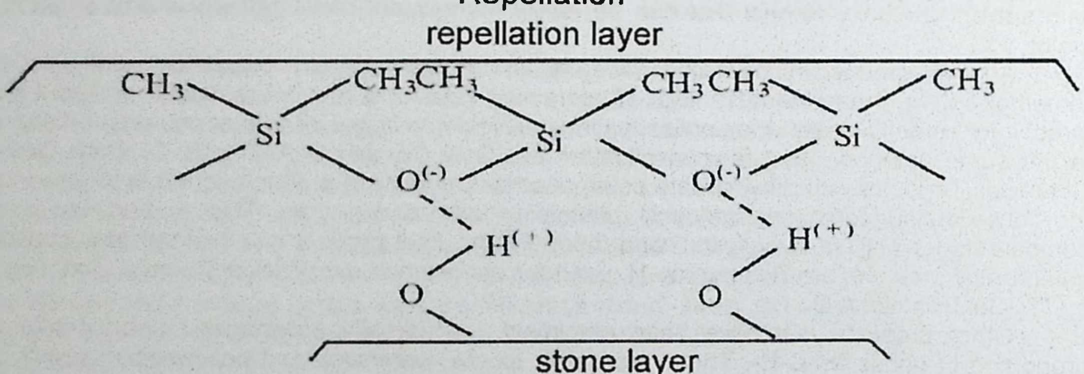
The aromatic compounds, in particular, lend larger elasticity to the polymers in comparison to the aliphatics. In contrast, the aliphatics are more resilient to ultraviolet rays. The most noteworthy products in this category are Rhodorsil XR-893 and Rhodorsil 11309, which are both methyl-phenyl-polysiloxans and are both by Rhone Poulenc. Rhodorsil XR-893 has been used for consolidating marble and limestone materials, while Rhodorsil is either being used on its own, or being added to a hydrophobic substance, typically methyl-silicate.

The following diagrams illustrate both the consolidating and the hydrophobic qualities of silicon polymers:

Consolidation



Repellation



Joining together and sticking of fragments.

The methods of joining, filling and aesthetically restoring the archaeological findings and architectural structures encompass the employment of materials that are both compatible and reversible, in line with the international standards in monuments' conservation and restoration. In particular, specialist mortar and pigments were utilized for the replication of ground levels in the color and the texture of schist, as indicated by the physiochemical analyses that had been previously conducted.

The aesthetic restoration of an architectural structure takes place towards the end of the repositioning process and includes the joining of fragments, together with the filling of openings, cracks, splits, or missing parts and places of joining. In order to join detached fragments, a solder material can be used on its own or in combination with certain abutments.

The use of metallic dowels in order to support a union is a very old conservation method, while the material most commonly employed used to be iron. However, iron gets easily oxidized in the presence of water, causing severe damage to the ancient objects. This is because of the increase in the volume of the dowel in the aperture, and the formation of oxidization products and their breaking down on the surface and in the pores of the material. Dowels made of copper alloys, which were more commonly used than the iron ones, also get oxidized with time.

During the last few years, the employment of other metals, such as titanium or stainless steel is favoured. These two do not get oxidized and therefore offer better stability to the union. The metallic dowel is frequently enclosed with a suitable structural solder or even with mortar. In earlier years, lead used to be employed for that purpose, while more recently special epoxy resins have been used. These resins protect the metal, as they prevent its contact with water, which penetrates the porous structure of the material. Dowels made of epoxy or polyester resins are utilized in the joining of light fragments. These dowels resemble glass bars and have the advantages of being very light, being relatively chemically stable, and being resistant to traction. Their limitation is the big difference in thermal expansion coefficient in relation to the original material.

The following process has been followed during the joining of fragmented objects:

An aperture is made in the centre of every fragment; more apertures can be made on a fragment should its surface or weight be large. The apertures are made symmetrically on the surface of the two joining surfaces; and care is given in order for the aperture patterns in the two surfaces to coincide so that the dowel can fit. In order to achieve perfect match of the apertures, an aperture is initially made in one fragment with the use of a non-shock drilling machine. Then, two diagonal lines that intersect exactly at the centre of the aperture are designed on its surface. The second fragment is placed on top of the first, with the two surfaces facing each other. The edges of the lines on the first fragment are marked on the surface of the second fragment, and the lines are then designed. The exact spot where the lines intersect specifies the second aperture. Another method is to place a small quantity of wet clay on the area of the first aperture, and then press it against the surface of the second fragment, thus identifying the place where the second aperture should be made. In order to achieve higher accuracy, a small aperture is initially drilled, which gets larger by gradually increasing the size of the drill nose. The size of the aperture depends both on the robustness of the material, and the width of the surface around the aperture.

In the instance of one fragment being larger than the other, a slightly larger aperture is drilled in the smaller piece. In this way, the backlash that has potentially been created in the dowel gets corrected, and the two pieces fit perfectly together. In cases of both pieces being equal in size, a larger aperture is drilled in either of them. The dowel is regularly made to be "thorny" with the use of a file, saw, or wheel, in order to achieve better grip. Both surfaces are cleaned before drilling, and, if completely flat, they are given a tap with a sharp tool in order to attain a slightly rough surface. After drilling, the apertures are meticulously cleaned. One of the apertures is then filled with either mortar or the consolidator, the dowel is being inserted, and it is left to dry. When mortar is being used, a pulp dipped in distilled water is placed around the aperture where the dowel has been inserted. More times than not, some of the dust from drilling is added to the mortar or consolidator in order to achieve both a stronger union and color fidelity. The mortar or consolidator is spread inside the second aperture and on one of the surfaces to be joined, and the two fragments are pressed together. The extra mortar or consolidator that has leaked after pressing is carefully wiped. The mortar or consolidator is then left to dry; in the case of mortar being used, a pulp dipped in distilled water is placed over the joint. Finally, when mortar has been used, a piece of sandpaper is placed over the joint and is tapped lightly, so that the joint resembles the texture of porous material.

Filling of cracks, empty spaces, missing parts and areas of joining.

The materials used for filling have to be binding and inert, with similar qualities to the original material in regards to their color, porous surface and mechanical resistance.

Powdered glass or quartz or dust from the original material are commonly used as inert material. In order to attain the desired color, the addition of a small amount of inorganic pigment is possible, as long as this is chemically stable. In cases where strong mechanical resistance is not desirable, limestone grindings are used as inert material. The diameter of the filler grains is determined according to the pores and the homogeneity of the original material. The filler for a material with small pores needs to consist of small diameter grains with a small range of granular size; while, for materials with larger pores, the filler grains need to be medium-sized and varied.

In order to fill in large missing parts, a copy of the missing part needs to be constructed, where the filler is cast. When the original object is symmetrical, a part of the object that is similar to the missing one is copied in mortar. In this case, soap water or a thin layer of talk is placed between the original object and the mortar. Alternatively, the cast is produced in silicon rubber.

When the surface of the original material is crumbling, a sheet of special paper is applied on it and pressed down with a brush dipped in distilled water. The cast is made in parts, let to dry, and placed at the part that is missing. Should the cast be lined in paper, a special varnish is used in order to seal it before it is filled with the mortar; while silicon casts do not get insulated. The parts of the surface of the original material that will contact the mortar are lightly hammered with a sharp tool in order to achieve better binding with the mortar. A joint is often inserted partly in an aperture in the original material and partly in the mortar. A special vibrator is placed inside the cast when the mortar is being poured, in order to prevent the formation of air bubbles.

When the missing part cannot be copied from an already existing symmetrical part of the original object, a dummy is made from plasticine or clay or mortar. A replica of silicon rubber cast is taken from the dummy (negative) and is placed at the missing part area. Mortar is then poured into the cast (positive). In some cases, the positive is created separately and then secured at the missing part area.

Fig. 1. The archaeological site before conservation.

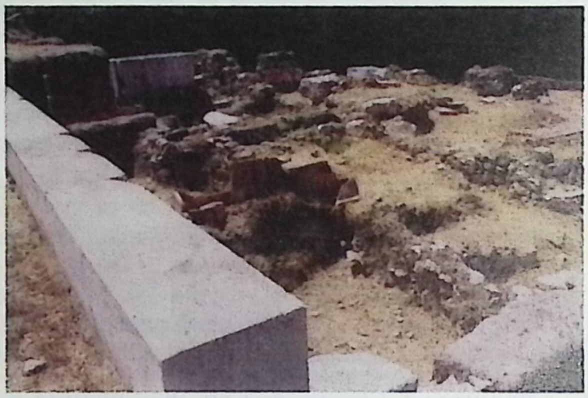


Fig. 2. The archaeological site before conservation.

Fig. 3. The archaeological site before conservation.

Fig. 4. Consolidation of surfaces and gap filling of missing areas.

Fig. 5. Consolidation of surfaces and gap filling of missing areas.

Fig. 6. Consolidation of surfaces and gap filling of missing areas.

Fig. 7. Consolidation of surfaces and gap filling of missing areas in kiln for ancient ceramics.

Fig. 8. Imitation of the sides of the archaeological site.

Fig. 9. The Acharnian Way after conservation.

Fig. 10. Consolidation of surfaces and gap filling of missing areas in carnivorowses.

Fig 11. Consolidation of surfaces and gap filling of missing areas in kiln for ancient ceramics.

Fig 12. Consolidation of surfaces and gap filling of missing areas in carnivorowses.

Fig. 13. The archaeological site after conservation.

Fig. 14. The archaeological site after conservation.

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