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Conservation of the Plaster at the Lavriotike Ore Washeries

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Abstract Mineral ore exploitation of the Lavreotike in southeast Attica reached its apogee in the 5th-4th centuries B.C. with silver revenues from the site contributing to the glory of the Athenians. The most impressive testimonials to centuries of mining activity are the vestiges of hundreds of washeries, where a novel way of ore purification was introduced: the metal rich concentrate was gravitationally separated from waste through washing. A smooth waterproof plaster covers these ingenuous recycling structures, which were vital in the semi-arid environment where water was so scarce it had to be conserved and reused as efficiently as possible. Conservation work at the archaeological site of Ag.Triada focused on the repair of the lead-rich hydraulic plaster of four rectangular washeries. Exposure to the elements (frost, rain) led to the disaggregation and subsequent loss of both the plaster and tailings (plynites). Thorough analysis of authentic plaster (mineralogical/petrographic, chemical analysis, porosity, strength and granulometry) led to the design of compatible repair mortars, used to stabilize the weathered plaster.

1 Introduction

The Lavreotike, which spans the southeast tip of Attica, is rich in minerals and ores, the most important of which are galenite and cerussite which were exploited to produce silver and lead. Copper ore was repeatedly mined at the site from the prehistoric period, through the proto-Byzantine period, until the turn of the last century; the mining of silver is inextricably related to the glory of classical Athens, the revenues of which financed many projects, including the construction of the Acropolis monuments and the city’s naval fleet. The indicative yield of lead was approximately 17.5% and of silver 350 gr/ton [1].

The geological stratigraphy of the area is fairly uniform. Layers of white marble overlay layers of schist in three formations of variable thickness and direction. The mineral bearing contacts existed in pockets at the interface of
marble and schist. The third/lower contact, which was tapped into by the Athenians, lay at a depth of approximately 100 m [2].

The Ag.Triada site which lies in the upper reaches of the Legrena valley, 150-165m above sea level, features a system of washeries, cisterns and workshops. The site lies approximately 2 km from the bays of Sounion and Perdika and the modern day city of Lavrion. The climate is temperate with limited rainfall (200-500mm/yr). The median temperature is 10°C in winter and 28°C in summer. Winds are mostly of N-NE direction.

A typical rectangular washer is comprised of a wide, shallow stand tank separated from a working floor by thin stone slabs with funnel-shaped holes at half their height. The working floor, which is approximately the same width as the stand tank, is either level or gently sloping downwards. It is separated from the drying floor by one of four channels which outline the drying floor. The gently sloping channels connect two deep sedimentation basins at the far corners of the drying floor and lead back to a re-bailing basin often adjacent to a platform.

Initially the ore was manually sorted and the fragments rich in lead were sent to the furnace, those with less than 20% were sent to the washer. The washing activity (purification/separation) consists of a series of events. The ore was ground and separated gravitationally through the use of running water in the stand tank. Running water swept away all grains which did not contain argentiferous (silver bearing) lead. When the water in the tank became murky, the holes were unplugged so that it could flow into the first channel and then counter-clockwise through the channels and basins into the final rebailing basin, cleaning itself in the process [3, 4].

2 The materials

The washeries were partly hewn from the rock and partly constructed from local marble, schist and limestone in the trapezoidal rubble masonry system, where two of the four planes of the blocks are parallel, and voids were filled with stone chips. The technological innovation lay in the manufacture of an impervious, dense and durable plaster which allowed for the efficient collection and recycling of water. It has been estimated that for the concentration of each ton of ore, 10 tons of water were required [5]. The lead-rich lime plaster has been the subject of numerous studies [6, 7]; the CaO-PbO-SiO₂ system is basic to all syntheses involved in plaster production because of the close association of marble, quartz and lead compounds [8]. It was applied in a single coat approximately 2cm thick and was seen to contain a coarse aggregate with a medium grain size of ø9-10mm. Preserved to this day in great expanses, the plaster is dense and smooth with a good adherence to the masonry construction. Transitions between the vertical and horizontal planes were made with uniform rounded edges.
A waterproof dark surface layer is found on plasters lining both washeries and cisterns. It is thought to have been produced as follows: a mixture of litharge, the by-product of cupellation, and ekvolades (discarded ores which are poor in lead, copper or zinc oxide) was melted in a furnace to form a glassy substance which was ground to a fine powder. It was added to slaked lime and applied to the plaster surface in layers which were approximately 100-200\(\mu\)m thick; the colour is attributed to the presence of zinc and manganese oxides [9].

Tailings/plynites - the sedimentation products gathered in the washeries - have been preserved on the horizontal surfaces of the working and drying floors, in layers/piles approximately 1.5-3cm thick. They are macroscopically identified by their reddish brown colour and their grainy texture. The discarded material, solidified on the floors, is embedded in a matrix of clay minerals, calcite and iron oxides [10]. Tailings often separate from the plaster surface due to differences in thermal expansion and weathering patterns.

3 Condition

The abandonment of mining activity around the 1\(^{st}\) c. B.C., despite sporadic reuse and a brief come back in the 19\(^{th}\) century, has led to the deterioration of the physical remains. Structurally speaking, the four washeries in Ag.Triada remain in good condition barring the occasional displacement or disappearance of ashlar blocks often from the edges of the floors. The cause of such a loss is due to both human (negligence, vandalism) and natural factors (vegetation).

Exposure to the elements over the millennia has compromised the integrity of the extraordinary plaster; once the material has been undermined, the rate of weathering is by no means linear. Disruption of the matrix (cracking) is most often observed at the edges of the floors and erosion proceeds inwards so that the loss of the plaster is most pronounced on horizontal surfaces (Fig.1). The evolution of weathering is clearly seen in the different stages ranging from the loss of the outer smooth surface of the plaster and exposure of the aggregate, to complete disaggregation of the mortar which remains on the floors as gravel. As a result, the plaster is better preserved on the more protected, internal vertical surfaces of the channels and basins. Cracking, delamination and internal voids are attributed to the combined effect of water ingress and mechanical stress induced by roots.

Frost damage seems to be the primary weathering mechanism resulting from exposure to the elements, along with temperature and humidity fluctuations. Soil entrapment, on horizontal surfaces but also in discontinuities of construction within the masonry, provides a constant source of water that is subjected to freeze-thaw cycles. In addition, the expansion and contraction of the soil’s clay inclusions further disrupts the plaster matrix.

The conservation proposal focused on the selection of compatible mortar and grout mixes for the consolidation of the plaster and tailings. In order to curtail loss
it was deemed necessary to: point the edges of the well-preserved surfaces, infill small lacunae with mortar, grout internal voids and re-attach delaminations by correcting deformation and apply a consolidant/water repellent to eroded areas.

Fig. 1 Plaster at the edges of the floors is most prone to deterioration caused by water ingress.

4 Experimental program

The experimental program was devised to complement previous findings on authentic plasters and tailings in order to design compatible repair mortars in terms of composition, appearance and characteristics related to durability. Analysis of authentic plasters included mineralogical/petrographic analysis (XRD and thin section observation under a polarizing microscope) simple mortar analysis [11], chemical analysis, porosity measurements with a Mercury porosimeter and analysis of compressive strength [12], grain size distribution [13] and water absorption at saturation [14].

Authentic plasters are lime-based and contain coarse to medium-sized aggregates (0.6-2.5mm) produced with a binder to aggregate ratio of 1:1 to 1:2. The lime was probably created locally [8] with the aggregate being obtained from the area, as is indicated by the presence of cerussite and fluorite identified in the mineralogical analysis, underlining the innovative and efficient organization of the mining activity. It was observed through microscopy and simple mortar analysis,
that the tailings were used as an aggregate in the plasters of most washeries. Interestingly, the plaster of washery N°4 which predates the three others portrays different characteristics, indicating a constantly evolving mortar technology. All washeries feature plaster with low total porosity values (7-16%), tensile strength in the range of 0.2-1MPa, low water absorption at saturation values (10-12%), high hydraulicity indices, and a significant presence of lead (4-5%) and other heavy metals (Pb, Ag, Cd, Zn, Mn) located 5-15mm from the outer surface [15]. Plaster from washery N°4 features an aggregate which consists of rounded grains gathered from the nearby streambed and a small quantity of brick powder. It has a higher total porosity (22%) and water absorption value at saturation (16%) but has a lower incidence of Pb (0.2%). The tailings feature a higher apparent specific weight, low porosity value (10%) and a very low water absorption value (3.9%).

Based on these findings, two mortar mixes (LA2 with a median grain size of ø1mm and LA5 with a median grain size of ø0.5mm) were designed. The coarse grained mortar was designed for deep infills or edging of plaster layers >2cm in thickness. A natural hydraulic lime with pozzolanic additives (NHL-Z 3.5) by Lafarge was used as the binder which was mixed with a variety of aggregates (siliceous sand, brick powder), chosen for their colour, composition and grain size, to a binder aggregate ratio of 1:3. The grain size distribution of aggregates was thoroughly examined as good packing makes for dense, durable mortars. Optimum water quantity was selected on the basis of workability. Consolidated samples with OH100 treated with water repellent BS290 by Wacker Chemie were also evaluated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binder and Aggregate</th>
<th>B/A ratio</th>
<th>Water/Binder ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA2</td>
<td>River sand 0-4mm</td>
<td>1:3 by weight</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>Brick powder 0-2mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Siliceous sand 1-7mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydraulic lime NHL-Z 3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LA5</td>
<td>River sand 0-4mm</td>
<td>1:3 by weight</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>Brick powder 0-1mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Siliceous sand 0.1-1mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydraulic lime NHL-Z 3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DA2</td>
<td>Pozzolan</td>
<td>8:2 by weight</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>Hydraulic lime NHL-Z 3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The testing program for the repair mortars included measurements of specific apparent weight, porosity, water absorption by saturation, water absorption rate and coefficient [16], permeability measurements [17], compressive and tensile strength [18] and durability testing with sodium sulphate immersion cycles [19].
Porosity measurements at 28 days were 16% and 17% for the coarse and fine-grained mix respectively with comparable water absorption at saturation values as those of authentic plasters (10.5% and 12.4%). Both mortars once subjected to sodium sulphate tests proved durable; at 45 cycles they had retained their shape and roughly maintained their original weight. Consolidation decreased water absorption while retaining permeability.

In addition, a hydraulic lime grout containing hydraulic lime NHL-Z 3.5, a pozzolan and a plasticizer, was tested. At 90 days, compressive strength reached 8.4MPa and tensile strength reached 2.6MPa. Segregation was <2%.

**Table 2** Properties of authentic plasters, tailings and repair mortars

<table>
<thead>
<tr>
<th>Sample</th>
<th>P (%)</th>
<th>Rm (μm)</th>
<th>CC ((g/cm^2s^{1/2}))</th>
<th>AS Wt (%)</th>
<th>WVTR ((g/cm^2d))</th>
<th>ASW ((g/cm^2))</th>
<th>CS (MPa)</th>
<th>TS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA3k</td>
<td>7.4</td>
<td>0.09</td>
<td>7.6</td>
<td>2.1</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
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<tr>
<td>LA3k1</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>LA4k</td>
<td>22.3</td>
<td>0.1</td>
<td>16.2</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA7k</td>
<td>13.6</td>
<td>0.1</td>
<td>10.5</td>
<td>2.1</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
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</tr>
<tr>
<td>LA2k</td>
<td>15.3</td>
<td>0.1</td>
<td>12.6</td>
<td>2.1</td>
<td>-</td>
<td>0.2</td>
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<tr>
<td>LA6k</td>
<td>16.2</td>
<td>0.2</td>
<td>9.6</td>
<td>2.4</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA3p</td>
<td>10.1</td>
<td>1</td>
<td>3.9</td>
<td>2.6</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA2</td>
<td>16</td>
<td>0.1</td>
<td>10.5</td>
<td>14.8</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA2-s</td>
<td>-</td>
<td>0</td>
<td>0.5</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA5</td>
<td>17.7</td>
<td>0.1</td>
<td>12.5</td>
<td>8.4</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA5-s</td>
<td>-</td>
<td>0</td>
<td>0.8</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

*tailings **repair mortars treated with a consolidant and water repellent


5 Conservation Interventions

The scope of the conservation proposal addressed primarily the stabilization of plaster in the washeries. Cleaning with both dry and wet methods was undertaken in order to remove all loose debris and deposits from the surfaces. Pumps were used to empty stagnating water from channels and basins.

Grouting of internal voids and reattachment of delaminations also required diligent cleaning. A gauze facing was applied to the cleaned plaster surface with a 5-8% solution of Paraloid B72 in acetone in order to avoid cracking and/or bulging. Soil accumulation and debris were removed by aspiration and brushing followed by water spray. Flexible tubes of Ø 2-4mm and needles were inserted into cracks or into the sides at different depths and were attached in place with the
pointing mortar (Fig. 2). Grouting was performed manually using plastic syringes which proceeded from the bottom upwards; it was monitored through the tubes, some of which acted as exit holes. A metal strut with revolving head was used over separation layers (rubber, foam and polyester film) in order to apply pressure to the injected area. The grout was mixed in a 5Lt ultrasonic mixer to increase injectability and stability. The tubes were removed 3-4 days after grouting, and the entry/exit holes were filled with mortar.

Edging and filling of small lacunae with mortar often necessitated the detachment and re-setting of a section’s peripheral fragments with little or no adherence to the substrate, due mostly to the accumulation of soil and microorganisms/roots. In cases where the plaster edges were frayed and some soil and/or roots remained at the interface of the masonry substrate and plaster, stone chips were used as galleting in order to provide a solid backing for the edging mortar. Lacunae exceeding 3-4cm in depth were filled with layers of mortar and stone chips. Mortars were kept moist in order to ensure adequate curing.

Fig. 2. Washery working floor with remnants of plaster and tailings during grouting

The pilot conservation program of four washeries in the site of Ag.Triada was part of an extensive project to develop the area into an archaeological site by the archaeologist E. Kakkavogiannis, who has devoted much of his life to the Lavreotiki, and his team under the direction of the Ministry of Culture. Plaster
conservation will ensure the longevity of the washeries as evidence of ancient mining technology.

6 References

13. EN 1015.01 Methods of test for mortar for masonry- Part 1: Determination of particle size distribution (by sieve analysis)
16. Normal 11/85 Assorbimento d’acqua per capillarita
17. ASTM E96-80 Standard test methods for water vapour transmission of materials
18. EN 1015.01 Methods of test for mortar for masonry- Part 11: Determination of flexural and compressive strength of hardened mortar
19. Commission 25-PEM, Test No V.1b. Sodium sulphate immersion cycles