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A new mortar from a strange ancient mortar

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Abstract – During the restoration of Perseus, a sculptural complex realized by G. B. Pieratti in the XVIIth century sited in Boboli Garden (Florence), an ancient mortar used as glue of iron pivots with very particular characteristics was found. Indeed this mortar was made of a magnesium hydroxide based binder (brucite) and barite (barium sulphate) as aggregate. This mortar still show excellent conservation conditions. The aim of this work was trying to reproduce the ancient mortar according to the analytical data about its composition.

Key-words: Ancient magnesian mortar, recipe, Boboli Garden, new mortar.

I. INTRODUCTION

The statue of Perseus (Figure 1), is a sculptural complex sited in the pond of the Boboli Garden (Florence, Italy), park of Pitti Palace residence of Medici family. The statue was realized by Giovan Battista Pieratti in the 30th of the XVIIth century in the context of the expansion of the Boboli Garden [1]. Perseus was made with fragments of ancient Roman sculptures following the fashion of the time. During the expansion of the Boboli Garden, numerous fragments of statues from Roman villas owned by the Medici family came to Florence to be used in other works [2],[3]. Indeed the restoration of the Perseus (Opificio Delle Pietre Dure 2006-2009) (Figure 2), highlighted different materials and techniques utilized in its realisation which extended over a long period of time (from the first half of the XVIIth century until the 80s of the XXth century). It was possible to identify different types of adhesive products: mortars, synthetic resins and numerous pivots (ranging from copper to stainless steel). One of the mortars studied, showed excellent condition of conservation and strength of adhesion [4]; this is very interesting because the sculpture was placed in the pond in conditions of partial immersion and showed high

degradation phenomena due to the combined action of physical, chemical and biological factors.



Fig. 1. The pond in the Boboli Gardens (Florence, Italy) with Perseus.



Figure 2. The sculptural complex after the restoration.

Then the aim of this work was trying to reproduce this particular mortar, according to the analytical data, even in absence of the old recipe.

II. THE ANCIENT MORTAR

The ancient mortar analysed in a previous work [4] showed particular characteristics.

The raw materials utilised to produce this mortar seem to be:

- a Mg rich binder made of brucite $Mg(OH)_2$, obtained by burning magnesite $MgCO_3$, in order to obtain MgO, then slaked in water;
- an aggregate constituted by barite and impurities of micritic calcite, iron oxides and quartz; besides agglomerates of brucite and hydromagnesite of the binder are present with aggregate function.

In a magnesian binder usually the carbonation of $Mg(OH)_2$ is always incomplete due to its low solubility and it reaches only the stage of hydromagnesite (sometimes the carbonation does not take place or it develops very slowly in a partial way) [5]. Nevertheless the cohesion reached by the binder is very good thanks to the interlaced fibers structure of both brucite and hydromagnesite.

The particular characteristic of this ancient mortar is the use of a binder allowing the protection of the pivots from oxidation (Figure 3) thanks to the basic environment guaranteed by $Mg(OH)_2$ which carbonates with difficulty.



Figure 3. Particular of the ancient whitish adhesion mortar.

III. THE REPRODUCTION OF THE NEW MORTAR

Two types of mortars were realized according to the analytical data: barite ($BaSO_4$) coming from Società Mineraria Baritina S.p.a. - Storo (Trento) was used as aggregate, while for the binder, a powder of MgO was utilized (Figure 4):

- mortar A: MgO mixed with deionized H_2O as binder and barite ($BaSO_4$) as aggregate: the binder/aggregate ratio is 1/4;
- mortar B: MgO mixed with deionized H_2O as binder and barite ($BaSO_4$) as aggregate: the binder/aggregate

ratio is 1/5.

The grain size distribution of the barite aggregate is heterogeneous, between 300-400 μm and 1 mm. The curing time of the mortars has been five years.



Figure 4. The raw materials used to reproduce the ancient mortar: on the left the aggregate and on the right the powder of MgO.

IV. ANALYTICAL METHODS USED FOR THE STUDY OF THE NEW MORTAR

The following analytical techniques have been carried out on the new realized mortars [6], [7]:

- mineralogical analysis through X ray diffractometry (XRD) (X'Pert PRO by PANalytical with Cu anticathode and HighScore software for acquisition and interpretation of the data) according to the following operative conditions: $2\theta = 3-70$, time per step = 60.325 sec, step size = 0.033, 40 KV, 30 mA;
- petrographic analyses: transmitted light microscopic observation (Zeiss AXIO Scope.A1 microscope);
- pH measurements were carried out adapting the method suggested by [8]: the pulverized samples were obtained using an ultrasound bath. The pH measurements were conducted on the portion of the sample that was retained on the 100 μm sieve. The tests were conducted using 3g of sample with a dilution ratio of 1:2 (6 ml of distilled water).

The pH readings were obtained using both a pH probe with a digital meter (PCE-PHD1) and a pH strips (Macherey-Nagel Duotest pH 7.0-10 and 9.5-14.0);

- porosity accessible to water by means of a hydrostatic balance. The porosity accessible to water was determined on 3 specimens for each type of mortar. To determine this parameter the dry weight (P_s), hydrostatic weight (P_i) and wet weight (P_b) were measured. The specimens were placed in a stove at 60° C until the dry weight was reached, (i.e. when the difference between two successive

weighing at an interval of 24 h is not greater than 0.1 % of the mass of the specimen). Then the specimens were immersed in distilled water under vacuum for 24 hours and subsequently 24 hours more without vacuum. Thus, the hydrostatic and wet weight were determined. The porosity accessible to water (WP) was calculated according to the following equation (1):

$$WP\% = (Pb - Ps / Pb - Pi) * 100 \quad (1)$$

An analytical balance with four decimal places was used to determine the weights (Mettler Toledo model AG204) [9].

V. RESULTS AND DISCUSSION

The analyses realized on the two types of mortars highlighted an alkalinity of these (pH=9.7).

The XRD analysis of mortar A shows the presence of barite, brucite, hydromagnesite, and of quartz, magnesian calcite, dolomite, while mortar B, points out the presence of barite, brucite, hydromagnesite, besides quartz, calcite, dolomite, barytocalcite (see Table 1, Figures 5 and 6).

Table 1. Mineralogical composition of mortars (relative abundance: XXX=very abundant; XX=abundant, X=present; tr= trace).

Minerals name	Mortar A	Mortar B
Barite	XXX	XXX
Quartz	XX	XX
Brucite	XX	XX
Hydromagnesite	X	tr
Dolomite	X	XX
Barytocalcite	-	X
Calcite	-	X
Calcite magnesian	X	-

Some little differences between the two mortars can be emphasized: in mortar A there is no barytocalcite and calcite while in mortar B there is no magnesian calcite. The presence, in the mortars, of mixed calcium and magnesium carbonates, barytocalcite and quartz would suggest the existence of impurities in the raw materials, which are quarry waste of the Società Mineraria Baritina (Tn).

The porosity accessible to water for mortar A it is 42.7%

while for mortar B is 45.6%. This datum is in agreement with the lower cohesion of mortar B.

The petrographic analyses carried out on the ancient mortar of the Perseus showed a Mg-rich binder (brucite/hydromagnesite) and an abundant aggregate with two granulometric fractions (one with dimensions of 20-50 µm and the other 150-300 µm): the finer fraction is made of barite and magnesite/hydromagnesite, and the coarser fraction is made of brucite and hydromagnesite agglomerates. Moreover there are impurities of micritic calcite, iron oxides and quartz.

The mortar looks well mixed, with a binder/aggregate ratio of about 1/3 and a low porosity, constituted by rounded pores [4] (Figures 7 and 8).

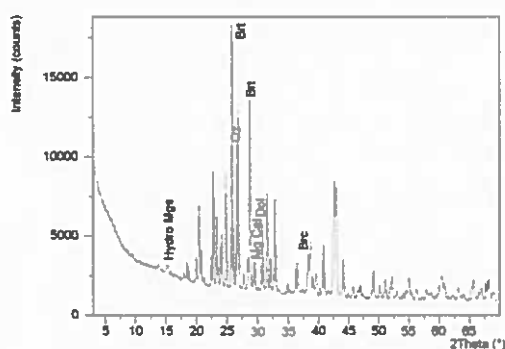


Figure 5. XRD pattern of mortar A. The main peaks of Brt: barite; Qz: quartz; Mg Cal: calcite magnesian; Dol: dolomite; Brc: brucite; Hydro Mgs: hydromagnesite are reported.

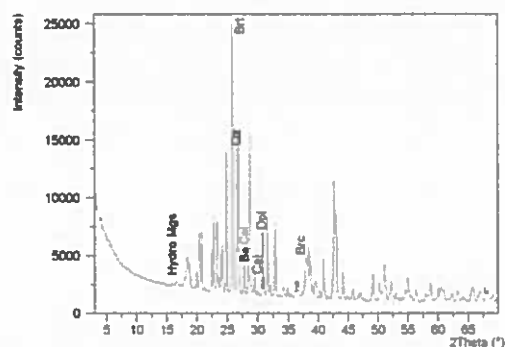


Figure 6. XRD pattern of mortar B. The main peaks of Brt: barite; Qz: quartz; Cal: calcite; Dol: dolomite; Brc: brucite; Ba Cal: barytocalcite; Hydro Mgs: hydromagnesite are reported.

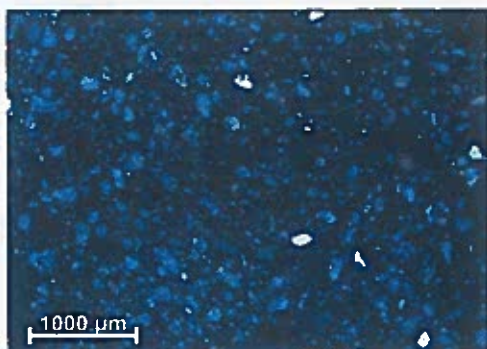


Figure 7. Image in thin section in xpl of the ancient mortar: an abundant aggregate with two granulometric fractions constituted mainly of barite and hydromagnesite is present.

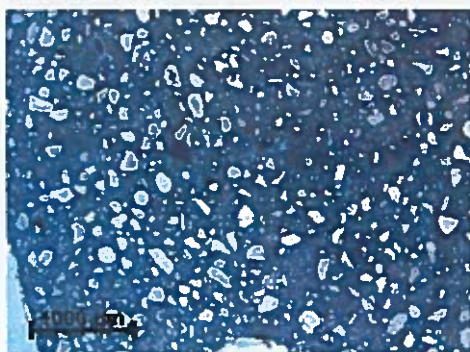


Figure 8. Image in thin section in ppl of the ancient mortar: an abundant aggregate with two granulometric fractions is present.

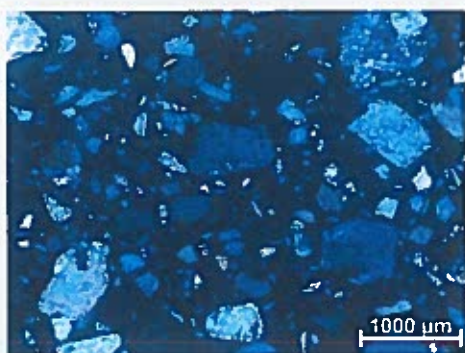


Figure 9. Image in thin section in xpl of mortar A: an abundant aggregate with two granulometric fractions constituted mainly of barite and dolomite is present.

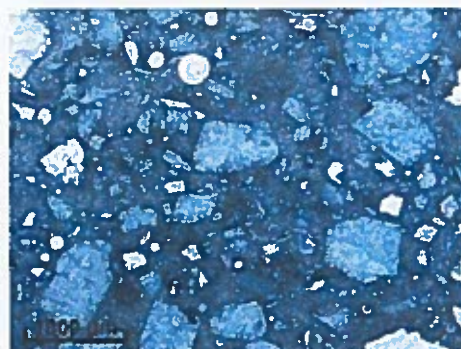


Figure 10. Image in thin section in ppl of the mortar A: abundant aggregate with two granulometric fraction is presents.

The petrographic analyses carried out on the thin sections of the new mortars showed very different characteristics with respect to the ancient mortar.

The mortar A shows an isotropic binder where is difficult to highlight the presence of hydromagnesite. The aggregate is coarse with a grain size ranging from 300-400 μm to 1 mm constituted of barite and dolomite; brucite is not detected (Figures 9 and 10).

The mortar B shows a binder where hydromagnesite is visible. The aggregate is more abundant and coarser compared to mortar A and almost lacking in the finer fraction. The composition of the aggregate is the same of the mortar A (Figures 11, 12 and 13).

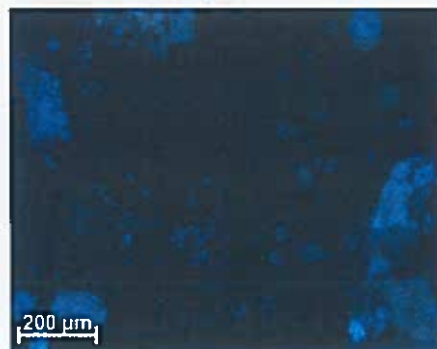


Figure 11. Image in thin section in xpl of the mortar B: hydromagnesite with subspherical shape are diffused in the binder.

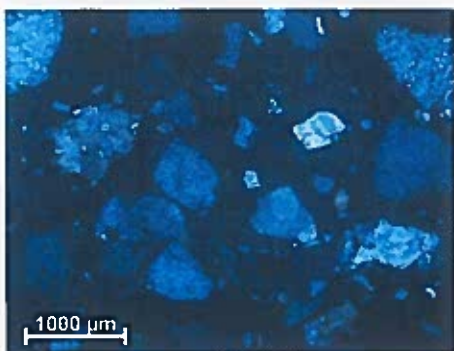


Figure 12. Image in thin section in xpl of the mortar B: an abundant and coarse aggregate is present.

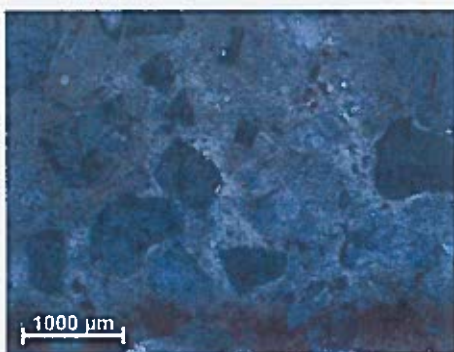


Figure 13. Image in thin section in ppl of the mortar B: an abundant and coarse aggregate is present.

It is noticeable that the ancient mortar showed different texture, grain size and binder/aggregate ratio. Besides, brucite was present while in the new mortars it is not detectable.

VI. CONCLUSION

The results obtained from the experimentation carried out to realize the two mixtures show that the new mortars show differences between them, above all porosity and cohesion; this could be referred to a different amount of mixing water (probably more water in mortar B showing an higher porosity); while the amount of finer aggregate in the mortar A could be responsible of a higher cohesion. Little differences are present in the composition due the presence of impurities in the raw materials.

The most relevant inhomogeneity observed between the new mortars and the ancient can be ascribed to textural and compositional differences. The data show clearly that the binder, the grain size and the composition of the aggregate is different. This proves that it is not easy to reproduce an ancient mortar, because it is difficult to find the original raw materials both for the aggregate and for the binder. As for the aggregate, the ancient quarries are

unknown and often the new materials are rich in impurities because coming from quarry waste. As for the binder: in commerce it is not easy to find products realized according the burning conditions of the old kilns (i.e. temperature and partial vapour pressure). Moreover the curing time of the new mortars, lasted only few years, probably is not capable to recreate the characteristics developed after hundreds of years.

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