REVERSE ENGINEERING: A PROPER METHODOLOGY FOR COMPATIBLE RESTORATION MORTARS

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Abstract

The authentic mortars, deteriorated by natural weathering, salt decay and corrosive action of polluted atmospheres, have to be replaced, while extensive use of cement and polymer-based mortars, give unsatisfactory results, due to the high content of soluble salts and the limited compatibility with the original components of the masonry. Hence, restoration mortars with characteristics as similar as possible to those of the materials to be repaired are searched out. In Greece, where the art of masonry and mortars flourished from the ancient years to Byzantium, a variety of hydraulic mortars overcoming the above problems and proving high bearing capacity, has been studied by the NTUA Materials Science and Engineering Dept., showing tentatively, that it is possible either to improve the characteristics of traditional lime mortars by hydraulic lime, or to reconstruct durable pozzolanic mortars by active aggregates and admixtures like crushed brick and powder. A reverse engineering approach is adopted, i.e. to check the working hypothesis arising from durable ancient mortars by several syntheses concerning various compositions and proportions. Certain criteria are set for the choice of the raw materials, based on Standards, as well as, a certain production procedure is adopted. The evaluation of the restoration mortars (thermal analysis, microstructure, mechanical properties) is based on the acceptability limits set by the historic composites. The performance of restoration mortars in the masonry on pilot and monuments' scale is evaluated, regarding mainly the adhesion and cohesion bonds developed and the masonry behaviour regarding salt solution capillary rise, percolation and evaporation. The restoration mortars contribution to the structures behavior under seismic loads is evaluated by determining the mechanical characteristics (flexural, compressive strength, dynamic and static modulus of elasticity) of the mortars, by determining the static and dynamic behavior of pilot masonries constructed by them.

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1. Introduction- Defining incompatible performance of restoration mortars

Historic mortars, have been either washed out, or crashed and deteriorated in the aggressive urban and industrial atmosphere of nowadays, or due to earthquake damages and mechanical stresses exerted within historic structures [1].

Restoration mortars of cement and polymer, which have been used extensively in the last century and especially the last decades, present a limited lifetime. The resulting strategy of the conservation of the restoration ('Restauro di Restauro'), which finds a dramatic paradigm in the today's conservation of the 1920's Evans' restoration of the Knossos Palace in Crete, which survived for 4 millenniums, is to be avoided. The reinforced concrete presents the disadvantage of a short lifetime of 70 years in a marine environment. [2]. The advent of the portland cement and polymers in the field of conservation was accompanied by a parallel increase of unsuccessful interventions as known by the available literature [3,4] and recent experiences. The existing data permit the assessment and evaluation of the modern restoration mortars' performance on the artistic and architectural surfaces and on the historic masonries by their prominent negative impacts disclosed:

a) at the interfaces between material and environment regarding the diversification or even the intensification of the decay mechanisms, due to different physico-chemical characteristics and potentials,
b) at the interfaces between original and restoration materials, regarding the discontinuities stresses and anisotropies developed within the structure, or at the surface, due to incompatible physico-mechanical and microstructural characteristics.

The performance of historic and restoration mortars have been studied comparatively to judge their longevity in relation to:

The compatibility to the wall constituents, as far as:

- the physico-mechanical and physico-chemical properties are concerned, which control the main function of the mortar, to bind the building units together and to provide a durable masonry. Historic masonry is a composite system. Its durability is related both to the nature of the single constituents and to the particular interaction between mortar and stone or mortar and brick. The adhesion between building units and mortar in all these complex systems can be really different depending on the interaction between binder and load bearing units under various operating conditions, regarding the environment and the structure [5,6] The adhesion and the durability of the masonry is influenced by workmanship and by the environmental conditions or the pollution. The environmental conditions (humidity, in particular) can play an important role: favoring the reactivity between the constituents inducing the disaggregation of the matrix, or modifying the kinetics of the hardening [7]. The study of the elastic behaviour of the mortars gives information on bonding between binder and bearing unit and to the aggregate / matrix interface governing compatibility of masonry materials on the masonry structure and allowing for continuous stresses and strains [8]. The crushed brick-lime mortars of Hagia Sophia and other Byzantine monuments due to hydraulic amorphous alkali-silicate formations display considerable mechanical strength along with longevity and may be considered as early examples of reinforced concrete. Allowing the structure to absorb energy without affecting its material properties irreversibly, which is not encountered in most modern masonry or concrete structures [9]. Modern mortars and adhesives are less porous than building stones and bricks, with higher values of hardness, mechanical resistance and thermal expansion coefficient attributing to them a performance rather incompatible to the original materials [10].

- the microstructural properties and the capillary systems are concerned, which control the behaviour of the masonry to the percolation and evaporation of the salt solutions within it [11]. The use of cement and polymer-based mortars, which believed to be more resistant than the traditional ones, gave very unsatisfactory results, due to the high content of soluble salts and the limited compatibility between these hard, impermeable materials and the original components of the masonry [12]. The very dense pore structure towards very small pore radii and the low porosity of the modern cement restoration mortars preferentially induces the percolation of the salt solutions to the original, more porous and of wider pore structures towards larger pore radii, building units, triggering their intense corrosion by salt decay [13]

Resistance of the composites to the environmental deterioration.

The degradation of historic mortars is attributed mainly to the chemical dissolution of the mortar matrix, i.e the calcitic binder and is known as the washing out of mortar joints, concerning specifically lime mortars [14]. The vulnerability of historic composites to the damage processes as acid attack or salt crystallization is defined by the physicochemical and the mineralogical characteristics of the mortars, their microstructure and the adhesion of the binder to the aggregates. In a reverse approach, the production of restoration mortars designed with a proper microstructure to diminish vulnerability to salt decay, should be required, since these systems are deemed as more compatible with the porous building stones than the modern cement. Hence, the study of the restoration mortar's behaviour in marine, industrial and urban centers becomes a priority need. Acid attack of cement generally involves expansions due to the ettringite formation, successively followed by the gypsum one, in the cracks which directly damages the masonry [15]. Consequently, when cement is used in restoration mortars, it infers sulphates to the masonry as an inner source of acid attack and efflorescences [1], irreversibly damaging frescoes or painted architectural surfaces, etc. [16]

Hence, the compatibility of conservation materials (repair mortars, grouts and consolidants) to the historic masonries becomes a critical factor for the design and production of appropriate restoration mortars.

2. Characterization and evaluation of historic composites

Historic mortars are composite materials, comprised of hydraulic or aerial binding material, or mixture of binding materials, aggregates - not always in crystalline form-and additives, passive or active, which react with the binding material and are modified during their setting, hardening and ageing, according processes not well known yet [17].

Historic composites concern “disturbed” systems, as in “service” for decades of centuries under severe mechanical and environmental loadings. Therefore, the characterization of such materials can be achieved by integrating properly [18] the results of the various methods of partial analyses [19, 20], in order to understand the procedures employed to produce the final composites and the nature of the bonds developed among its constituents.

Characterization of historic composites encounters the investigation of the fundamental properties and characteristics by the following methods and techniques:

Mechanical properties

The tensile strength (fmt,k) of small mortar samples by the fragments test method [21, 22]. The dynamic elastic moduli by in situ ultra sonic tests at various locations on the monument [23, 24].

Physical Properties

Gradation

Grain size distribution of single components by fractionation and sieving through ISO 565 series of sieves. The lowest fraction (<63 μm) is considered as the binder; although more of less significant quantities of finely grained aggregates could be sometimes presented in this fraction. Sieving permits to estimate comparative binder to inert ratios for the various mortar types [14].

Microstructural characteristics

Total porosity, total cumulative volume, specific surface area, bulk density, average pore radius as well as, pore size distribution, using intrusion mercury porosimetry (IMP) or the Non – Destructive Technique Digital Image Processing (DIP) on microscopical observations - and on the phenomena and mechanisms occurring within the pores by scanning electron microscopy (SEM) [11].

Mineralogical and chemical characteristics

a) X-ray diffraction analysis (to identify the mineral crystalline phases of the mortar matrix and the aggregates)

b) Optical Microscopy (for the petrographical - mineralogical characterization of the mortars’ constituents, as well as for microscopic observations on the different mineral phases in the matrix) [20]

c) Scanning Electron Microscopy (SEM) added by Energy Dispersive Analysis EDX (for microscopic observations on the microstructure and the texture of the mortars and for elementary semi-quantitative analysis) [25]

d) Spectroscopy like Infrared (FT-IR) (for gathering qualitative information from a chemical point of view on some of the characteristic substances contained in mortar (calcium carbonate, dolomite, calcium and magnesium hydroxides, gypsum, organic additives etc.) and the presence of salts (nitrates, sulphates, oxalates, etc.), Nuclear Magnetic Resonance when possible (NMR) (to determine silico – aluminate formations, etc.) [26]

e) Thermal Analysis as Differential Thermal Analysis (DTA), along with Thermogravimetry (TG) techniques for the determination of the degree and the rate, of hardening of the binders in terms of carbonation and formation of hydraulic compounds, which allows for the classification of the investigated sample mortar categories. Since aggregates are inert and do not display hydraulic components, thermal analysis of the total fraction allows for getting insights on the various mortar matrixes. In the case of thermal analysis of the mortars with active aggregates or admixtures, separation becomes necessary. [18, 27]

f) Determination of the Total Soluble Salts

Within this concept, data on historic composites arisen from a systematic research performed at a large number (approximately 400 samples) of ancient Greek, Hellenistic, Roman, Byzantine, post-Byzantine and later historic mortars and concretes sampled from Fortifications, Monasteries, Churches, Historical Buildings and masonry structures in the Mediterranean Basin.

Tables 1 and 2 report the data obtained from the tests performed, as mentioned above, permitting the identification of physico-chemical and mechanical characteristics of the most typical mortars encountered in ancient structures.[28]

Table 1. Chemical characteristics of historic mortars as deriving from thermo gravimetric analysis

Mortar type	Physically bound water (%)	Structurally bound water (%)	CO_2%	CO_2/structurally bound water
Lime mortars	<1	<3	>32	10, 7.5 – 10
Lime mortars with unaltered portlandite	>1	4 – 12	18 – 34	1.5 – 9
Hydraulic lime mortars	>1	3.5 – 6.5	24 – 34	4.5 – 9.5
Natural pozzolanic mortars	4.5 – 5.5	5 – 14	12 – 20	<3
Artificial pozzolanic mortars	1 – 4	3.5 – 8.5	22 – 29, 10 – 19	3 – 6

Table 2. Physico – mechanical characteristics of historic mortars

Mortar type	Cum. Volume (mm^3/g)	Bulk Density (g/cm^3)	Average Pore Radius (μm)	Specific Surface Area (m^2/g)	Total Porosity (%)	Tensile Strength (MPa)	Binder: Aggreg. ratio
Lime mortars	170-230	1.5-1.8	0.8-3.3	1.3-3.3	30-45	<0.35	1:4-1:1
Lime mortars with unaltered Portland.	105-241	1.8-1.9	0.03-6.5	1.7-10.6	20-43	0.6-0.7	1:2-1:1
Hydraulic lime mortars	90-230	1.7-2.1	0.1-3.5	2.5-13.5	18-40	0.35-0.55	1:4-1:1
Natural pozzol. Mortars	160-265	1.6-1.9	0.1-1.5	3-14	30-42	>0.60	1:5-1:1
Artificial pozzol. mortars	170-280	1.5-1.9	0.1-0.8	3.5-9	30-40	>0.55	1:3

The ancient masons applied intuition and fantasy for the solution of their problems and, even more, a whole understanding of the role of all constituents that are an integral part of composites microstructure. They based on their intuitive knowledge and non scientific experience on the selected and applied materials. The ancients instinctively followed ways of ecology and economy. They did not waste valuable materials when materials of low value satisfied the requirements of the performance. They found ways to exploit to the maximum the potential of the available materials. They produced reactive lime and invented by empiricism criteria different types of pozzolanic materials and organic additives.

The physico-chemical and mechanical characteristics of the examined composites could be served in order to define specifications for restoration mortars with similar properties to the original composites employed in ancient structures. However, to assure the compliance of restoration mortars to these specifications a design process has to be adopted. This process should concern the nature and the quality of raw materials in use, the ratio of the binder/aggregates, the gradation of the aggregates along with the maximum grain size and the potential additives in order to ameliorate rheological and mechanical characteristics. Moreover, it has to take into consideration the purposes that the mortars have to serve in the masonry and their resistance and durability to the actual environmental loads.

3. Criteria and Methodology for the selection of raw materials and the production of restoration mortar syntheses

Criteria for the selection of raw materials

The selection of raw materials is the determining step for the development of restoration mortars with the task to meet the criteria arising from the knowledge of the historic composites.

The raw materials that are more common to use for the production process are:

a) Binding materials: lime putty, hydraulic lime and cement.
b) Aggregate materials: sand of silicate composition and crushed tile.
c) Additive materials: natural and artificial pozzolanic materials.

The techniques and the tests of investigation employed for the physico-chemical characterization of the raw materials are the following:

i) Thermal analysis (Differential Thermal along with Thermogravimetric Analysis)
ii) X-Ray Difraction (XRD)
iii) X-Ray Fluoresence (XRF)
iv) Porosimetric analysis
v) Pozzolanicity test
vi) Determination of soluble silica (Reactive silica) (EN 196-2)
vii) Granulometric analysis (ISO 565)
viii) Specific weight measurement

The selection of the raw materials results from the research of the locally available materials in relation to the technical characteristics and the production technology of the materials.

Binding Materials

Lime putty. The lime putty should fulfil the following technical specifications:

- the raw material for the production of lime should contain at least 98-99% of $CaCO_3$.
- the baking temperature of the raw material for the production of quick lime should be around 900 ^oC in order to obtain micro-crystalls of CaO and a high specific surface area. While the actual production of lime with high temperatures (~1200 ^oC) produces macro-crystalls of CaO, with low specific surface area and difficulties related to the slaking of quick lime.
- appropriate slaked process of the quick lime for the production of the lime putty.
- the lime putty should not contain less than 94% of (CaO+MgO) and free water in the paste not more than 60%.

Hydraulic Lime. The hydraulic lime should accomplish the following technical specifications:

- the baking temperature should not exceed the 900 ^oC, for the above-mentioned reasons for the production of lime.
- the presence of C_2S and CA (where: C_2S: $2CaO.SiO_2$,CA: $CaO.Al_2O_3$)
- index of hydraulicity between 0.31-0.42 (properly hydraulic lime), i.e., $i = p_s+p_a+p_f / p_c+p_m$

Aggregate Materials

Silicate Sand**.** The sand should be pure meaning without extraneous compounds, mineral salts, clays, silts, etc. Moreover it should be of silicate nature because it infers higher resistance to mechanical loads and weathering phenomena. It should also present a wide range of grain size distribution in order to satisfy the technical requirements indicated by the reverse engineering process.

Crushed brick. Crushed tile should be used to its physical and physico-chemical properties. As far as its physical function is concerned the tile, in general, has small specific weight therefore the mortar produced is lighter than the mortar which contains only sand. Thanks to the specific characteristics of the ceramic, the mortar gains elasticity and shows a better behavior to the mechanical loads and earthquake stresses.

If the ceramics are baked in a certain temperature (<850 ^oC), in relation with their composition (Ca-poor or marly clays of intermediate Ca content), they could create chemical bonds on the interface, between $Ca(OH)_2$ and the ceramic surface.

Additive materials

Natural and artificial pozzolanic materials. A pozzolanic additive, on its own, cannot be used as a binder material, but because it reacts with $Ca(OH)_2$ it forms silico-aluminate compounds of Ca. The pozzolanic additive should fulfil the following technical characteristics:

i) The results taken from the pozzolanicity test must give a compressive strength greater than 5 N/mm^2.
ii) It should present a good percentage of reactive silica (i.e. greater than 20%).

4. Criteria and Procedure for the Evaluation of restoration mortars

Evaluation of mortar pastes

The optimization of the mortar pastes on the base of the water requirement and the proper workability should be searched out. The reproducibility of the preparation process should be attempted by tests in order to estimate the technical characteristics of the fresh mortars. The optimum workmanship should be decided in the basis of a low water request, a good workability of the mixture, an appropriate cohesion of the paste and an efficient applicability in a pilot masonry structure.

For the measurement of the technical characteristics of the optimum paste in order to have an appropriate reproducibility an International Standard should be used and the following tests should be performed:

- Determination of air content
- Determination of bulk density
- Determination of consistence
- Determination of retained water
- Determination of volume change upon setting

The tests for the measurement of the characteristics on pastes are adopted for reproducibility reasons. The table flow test adopted for the measurement of the workability gives results between 13 and 16.5 cm. The majority of the values are higher than of 14 cm showing pastes with a plastic consistence range, in all categories of restoration mortars.

The water requirement is to put in relation with the nature of the binder, additives and aggregates. The syntheses having as binder only lime putty present the lowest requirement in water and the highest requirement the syntheses with hydraulic lime. Intermediate values present the syntheses with binding materials lime-cement, lime-brick powder, lime-pozzolana. The syntheses having as aggregate only sand present a higher requirement in water in respect to those composed with sand-ceramic aggregates, independently from the nature of binder; this fact could be justified from the employment of ceramic aggregates saturated of water.

The specific weight is to put in relation with the nature and quantity of the aggregate, binder, binder-additive. The syntheses with only sand aggregate present the higher values in respect to those of sand-ceramic aggregates. For the same reason syntheses with additives presents the higher % of air content, when generally the other syntheses show very low values (2.5-3 %).

The water retention content presents very high values; the higher values regarding the syntheses only with sand aggregate and the lowest ones in the syntheses with sand-crushed brick.

In addition measurements regarding the adhesion between the mortars and the structural units must take place. By this way the appliance of the mortar is tested, as well as, the cooperation between the fresh mortar and the main structural unit of the masonry that the mortar will be applied. By this way also the setting is tested and valuable information can be found about the potential problems in setting in order to avoid them at the time of the application on the masonry. In this case the simulation of the natural environment is a very critical factor and the aim to simulate it could give much information about the right application of the mortars, as the laboratory conditions in most cases is different from the actual environment of the masonry.

Evaluation of mortars during setting and hardening

The pastes syntheses produced after the above optimization should be moulded and stored under controlled conditions, appropriate for the setting and hardening of the mortars.

In order to evaluate the various syntheses during the setting and hardening of the mortars, the following measurements should be performed:

Differential Thermal Analysis - ThermoGravimetry (DTA - TG) in order to estimate the kinetics of mortars hardening through the study of carbonation of the binder and the development of the hydraulic phases,

Porosimetry in order to estimate the change of the microstructure during hardening, and

Mechanical Strength Tests in order to estimate the strength of the mortar developed during hardening.

The mechanical strengths are directly related to the rate of hardening of the binding material. Hence the mortars with hydraulic lime admixed with crushed-brick present the highest mechanical strengths to those with aerial binder that present the lowest mechanical strengths, compatible though to the historic mortars' requirements.

The thermal analysis results, which render the evolution of the mortars during setting and hardening, shows that hydraulic lime mortars perform the fastest rates of carbonation while lime putty syntheses perform the slowest ones. All the other syntheses lay in between. As far as the structurally bound water (hydraulic water) is concerned, the highest amounts are observed on the hydraulic mortars with crushed-brick, which also explain why these mortars present the highest mechanical strengths.

The study of the microstructure shows the compatibility with the historic mortars. In all syntheses of restoration mortars, the microstructure is compatible, therefore the raw materials, as well as, the mixtures ratios give satisfactory results.

The results indicate that mortars, having hydraulic lime as binder material and being admixed with crushed brick, present a better behavior to those made with aerial lime, or lime-cement, or lime-pozzolanic additives. Final selection of the proper restoration mortars at the time of their full strength acquired will permit pilot application and in situ evaluation regarding compatibility and good performance on the masonry.

It is proved that historic masonries could be disturbed by the differential transport behavior of the material components and deteriorated by the consequently developed tensions at the interfaces. The compatibility of various repair mortars to the porous building materials must be evaluated by their performance in transport and evaporation, in terms of ionic/moisture/vapor transport, which is shown in relation to their microstructure. The acceptability limits, defined by the original materials, indicate the microstructural requirements that repair mortars have to fulfill, in order to be compatible and infer longevity to the masonry structures. According to these requirements, all the different categories of restoration mortars must be tested Microstructural parameters during hardening are determined by intrusion mercury porosimetry. and transport phenomena are studied (in terms of vapor/moisture permeability), to judge the compatibility of the various cement-based systems with the porous building materials of the original structures.

It is proved that the relationships between transport phenomena and microstructure, as well as transport phenomena [29, 30] and long-term durability control the behavior of the stones and respectively the behavior of the masonries on weathering process mechanisms. The salt crystal growth as weathering mechanism of porous stone on historic masonries [31] depends on the solution supply and the evaporation rate according to the microclimate and the effective porous structure. It is concluded from previous works [32] that the susceptibility of a porous stone to salt decay is a function of both mechanical and structural parameters, i.e. (a) compressive strength, (b) modulus of compressibility, (c) porosity and pore size distribution and (d) total internal surface area. On the scale of the masonries the mechanism takes place continuously on sandstones, as well as on mortars and their interfaces. Hence, the compatibility of the sandstones and mortars, in terms of mechanical and structural parameters, determines the homogeneity of the weathering processes. Incompatibility leads to the differentiation of weathering rates and mechanisms, and develops respectively durability problems. The durability of the monuments depends on the transport phenomena [33] within the systems of materials. The direct correlation between materials coefficients regarding transport phenomena and microstructural parameters has been investigated [30]. Total porosity and pore size distribution effect, according to Meng [29], transport phenomena coefficients and patterns such as diffusion coefficient, water absorption coefficient and water/vapor permeability. Monuments act as pilots of long term durability assessment and evaluation. The main requirement for long term durability for complex systems like masonry of sandstones with mortars as bearing elements is the compatibility of the microstructure, so that the transport phenomena will proceed as homogeneously as possible.

From combined microstructure investigation and correlation with the results arising from the capillary rise and evaporation tests in all mortar categories at the Laboratory of Materials Science and Engineering the following general conclusions can be mentioned: arises a relation between water absorption coefficient and specific surface area. More specifically, pores with radius less than 0.1 μm do not participate at the water absorption phenomenon. This result is in agreement with other research findings [34, 35, 36]. From the results of the Pore Size Distribution (PSD), according to the pore ranges, as the percentage of the larger pores increases, i.e. specific surface area decreases, the Water Absorption Coefficient (WAC) increases. This might be explained from the fundamentals of interfacial tension, where the smaller the pore radius, i.e. the greater the specific surface area, the higher the resistance that have to be overcome. The Effective Porosity can be estimated in terms of pore size ranges, which contribute to the Total Absorbed Water, during Capillary Rise Tests [32].

Finally there is a need for the correlation of all the parameters tested by multivariate analysis, in order to define the relation between the specific physico-chemical and mechanical characteristics, as well as the relation between the different characteristics and the raw materials used for the production of restoration mortars.

This procedure could create a database which can be enriched with new results and find the specific relation between materials and measured properties.

Conclusions

Up to now, as tentative guidelines for restoration mortars the proper binder to aggregate ratio and the aggregates gradation were conceived, either as estimated by the analysis of historic mortars or as deduced from historic sources, recent scientific research data, scientific references etc. From the analysis of the physico-chemical and mechanical characteristics of historic mortars as above, it is concluded that in several cases, historic mortars with the same ratio and gradation could be classified to different microstructural patterns or could be characterized by different cohesion and adhesion bonds, which are the determining factors of the performance of the mortars on historic masonries. Hence, the classification of each case under investigation to a well-distinguished category of historic mortars can be achieved only by the physico-chemical and mechanical characteristics estimated by the pattern type. This is due to the interference of the various technical characteristics of the raw materials used and the technological procedures employed for the mortar production. However, this range of characteristics varies and should be estimated for every area, as a function of its specific characteristics, i.e. the quality of the raw materials allocated in the area and to the application requirements, concerning the compatibility to the original building units, the purposes which the mortars have to serve in the masonry (joint mortars, plasters, etc.) and its resistance to the environmental loads acting.

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