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Properties and technology of the crushed brick mortars of Hagia Sophia

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Abstract

Within the framework of the collaboration between Princeton University (Prof. A. Cakmak), the National Technical University of Athens (Prof. A. Moropoulou) and Bogazici University (Prof. Ishikara, Prof. Erdik), the present work deals with material analyses of small samples taken from Hagia Sophia, a sixth century masonry edifice, in Istanbul, Turkey, coordinated with structural studies to provide insight to the structure ability to withstand seismic loads.

From thorough microstructural, mineralogical, chemical and physico-chemical analyses already performed at the NTU-A. Microscopic observations give ample evidence to products of boundary reactions. Reaction rims at the ceramic-matrix interface are dispersed in the form of veins along the matrix, as if they fill the vacancies and discontinuities of its structure. Fine to medium grained aggregates, mainly quartz and plagioclase, varying in % by surface, are embedded in the calcitic matrix.

The observed reactions could be probably attributed to calcium silicate formations at the interface among the brick fragment, acting as the silicate source and membrane, and the lime which alkalises the interfacial surface and causes the chemical reaction. The nature of these adhesion reactions of physico-chemical character depends both on the type of ceramic and the calcium hydrate content of the mortar and establishes its so called "pozzolanic" character.

Through the correlation of the acquired data, the resemblance between the Byzantine production technology of analogous mortars in Greece and the crushed brick mortars of Hagia Sophia is confirmed.

The present work is based on the methods of the X-Ray diffraction Analysis and thermogravimetric analysis performed both on the samples themselves and on their fractions after a physical separation. The results account for a possible technology of a "pozzolanic" mortar, where one part per volume lime (in the analogy of 1/1 hydraulic to calcitic lime) was mixed with 3 parts of aggregates- the one to three being crushed brick fragments, the other one sea sand, and the third one most probably fine pozzolanic sand. However, up to now, analytical techniques cannot provide directly technology information, let alone on the physicochemical interactions among the constituents of historic walls, as in the case under study. Hence, a reverse engineering approach is needed to reveal traditional technologies for the production of restoration mortars, simulating byzantine technologies. Consequently, restoration mortars resembling the original ones should be provided instead of the modern cement mixtures.

Introduction

Within the framework of the collaboration between Princeton University, Prof. A. Cakmak and the National Technical University of Athens, Prof. A. Moropoulou, the present work deals with material analyses of small samples taken from Hagia Sophia, a sixth century masonry edifice, in Istanbul, Turkey, coordinated with structural studies [1] to provide insight to the structure ability to withstand seismic loads. The church contains four great brick arches springing from stone piers that offer primary support to a 31-meter diameter central dome and two semidomes.

A preliminary analysis was made by Mainstone [2] and Livingstone [3] giving some useful data indicating the "pozzolanic" character of the mortar.

In previous works of ours [4], the advanced physico-chemical bonds, developed between ceramic fragments, were studied in relation to the relatively high mechanical strength of the mortar. The strength of the mortar was estimated through destructive tests on small samples and the elastic modulus was estimated through non-destructive tests in situ. The estimated density and elastic moduli consistent with those tests were used in a numerical structural model of the primary dome support system. The elastic moduli were adjusted to match with system mode shapes and frequencies identified from measured responses to recent low intensity earthquakes. The calibrated model was used to predict the measured responses. Stresses under simulated severe earthquake loading were estimated at the critical locations in the arches and were compared with the measured mechanical strengths.

Due to weathering phenomena [5], the original crushed brick mortars deteriorate and are replaced by stronger mortars though incompatible with the original structure as they are produced by more or less modern cement mixtures. Considering this incompatibility as a serious problem for the seismic protection of Hagia Sophia, Bogasizi University, Princeton University and the National Technical University of Athens signed a relative program agreement [6] focusing, as far as materials are concerned, on revealing the suitable technology for the production of restoration mortars resembling the original ones.

From thorough microstructural, mineralogical, chemical and physico-chemical analyses already performed at the NTU-A [7] on small mortar samples taken from the structure in order to characterize the properties of the crushed brick mortars of Hagia Sophia, the following have been already concluded:

Microscopic observations give ample evidence to products of boundary reactions. Reaction rims at the ceramic-matrix interface are dispersed in the form of veins along the matrix, as if they fill the vacancies and discontinuities of its structure. Fine to medium grained aggregates, mainly quartz and plagioclase, varying in % by surface, are embedded in the calcitic matrix.

The observed reactions could be probably attributed to calcium silicate formations at the interface among the brick fragment, acting as the silicate source and membrane, and the lime which alkalises the interfacial surface and causes the chemical reaction [8,9].

The nature of these adhesion reactions of physico-chemical character depends both on the type of ceramic and the calcium hydrate content of the mortar and establishes its so called "pozzolanic" character.

The penetration of lime into the ceramic and the consequent reaction transforms the microstucture of the ceramic by transferring the pore radii towards smaller pores,

decreasing the total porosity and augmenting the apparent density. The transfer of the pore radii towards smaller pores confirms the cementitious character of the mortar matrix, imparting high strength to the mortar, while the compatibility of the masonry bricks with the crushed brick mortar is proved.

Finally, through the correlation of the acquired data, the resemblance between the Byzantine production technology of analogous mortars in Greece and the crushed brick mortars of Hagia Sophia is confirmed [9, 10].

The present work is based on the methods of the X-Ray diffraction and thermogravimetric analysis performed both on the samples themselves and on their fractions after a physical separation.

As we have already proved [11], the simultaneous use of these methods [12] could complete the characterization of the mortar properties and could reveal critical elements concerning the technology of mortar production .

Sampling

Two series of samples are examined. The first concerns samples from the Van Nice' s sampling 30 years ago preserved at the Damparton Oaks Museum in Washington D. C.. The second concerns samples recently taken from the monument. From historic data on construction periods of the several parts of the monument, building materials of 6th and 10th century are distinguished. The samples of mortars are shown in the Table 1.

Table 1 : Sampling of mortars

Samples No	Location	Historic Period
Sampling on the monument		
1.1	North-western buttresses	later than 10th cent. byzantine/ottoman
2.1	North main Arch/west point	byzantine (6th cent.)
3.1	South-eastern abatement	byzantine (6th cent.)
W1	Fortifications of the city	later than 10th cent. Byzantine / Ottoman
Samples from the Van Nice samples-collection Oakbourn Mus. Wash.)		
1a matrix	crushed brick mortar adhered to a piece of stone (6th)	
1b matrix	crushed brick mortar in nodules	
2	Integral sample of crushed brick mortar (6th)	
5a	Fine grained crushed brick mortar (10th)	
5b	Friable crushed brick mortar (10th)	

Methodology - Experimental Procedure

Mortars seem to be simple systems but they are not ; in reality the lime is often accompanied by hydraulic components. The inerts used often interact with the binder and by so doing, the technologies of setting up are very diversified. These situations make the study of the mixtures rather complex, because it is difficult to distinguish the neoformation compounds from the oldest ones.

A basic approach is offered by the granulometric analysis, allowing separation of the mortar in its components, in which the finer fraction is richer in binder. On this fraction (<63μm), composition examinations should be carried out in order to define the nature and quantity of the binder in the mortar [13].

A physical separation of phases and granulometric analysis are performed on the same mortar samples by sieving, in sieves of diameters: 63μm, 125μm, 250μm, 500μm, 1000μm, 2000μm, 4000μm and weighting consequently.

Characterization of the mortar properties could be accomplished by the use of thermal analysis. DTA can be used to identify various component materials and observe the reactions associated with controlled heating of the mortar. This method reveals thermal transformations, which include dehydration, dehydroxylation, oxidation and decomposition. In addition, crystalline transitions can be observed, which are exothermic or endothermic in nature. In combination with thermogravimetric analysis (TGA), the mass of the sample is monitored (weight loss) as a function of temperature.

Concerning clay minerals, the endothermic peak around 100°C is due to moisture water, whereas those appearing at about 200-250°C are attributed to "bounded water" or to "hydrated interlayer cations". Gypsum, if present, also shows endo-thermic effects within the range of 120-200°C.

The most common clay minerals (kaolinite, illite, smectite) are recognizable for their relatively strong endothermic effects within the range 500-650°C, followed by dehydroxylation. The DT and TG analysis identify the dehydration of calcium aluminosilicate phases giving clear evidence of a cementitious mortar rather than of a pure lime one. The phase transformation of quartz a-->b is detected at about 580°C. Also organic matter (eventually used as an additive to promote carbonation and to improve workability, setting time and durability of the mortars) can produce exothermic effects within the range 300-500°C.

Carbonates show distinctive endothermic peaks at around 840°C (Calcite) and a double one at around 780°C and at 860°C (dolomite), whose position may vary depending on grain size and other concomitant factors. They are due to the escape of CO2 during the breakdown of their structure.

Weight losses at reaction temperatures, transferred more or less near 700°C, render the loss of CO2 not from pure CaCO3 but from recarbonated lime which includes some cementitious materials, just in case that the original limestone contained suitable clay minerals the hydration of which might have contributed to the C-A-H or C-S-H phases.

Studies of the medieval mortars from the Gothic Cathedrals of France give evidence to early decomposition of CaCO3 to CO2 between 663-713°C, revealing that illite, present in the Paris basin, became dehydroxylated during the lime burning process. These dehydroxylated clays have acted as a "pozzolan" imparting early strength to the mortar. However, a more complex phenomenon occurs in a crushed brick mortar, since compounds of hydraulic type take place at the brick matrix interface as well.

DT and TG analyses identify the dehydration of calcium alumino-silicate phases, giving clear evidence of a cementitious mortar rather than of a pure lime one.

Thermal analyses are performed by a Mettler TG 50, Thermo Balance, thermal analyzer system. The equipment monitors the weight loss of the mass of a 20-50 mg

sample, when submitted to controlled heating from the environment temperature up to 1000°C (30-1000°C).

Simultaneously, the values of the derivate of the weight loss in function with the time of heating are registered, where the main transformations (weight losses) occur.

However, the value of the temperature depends on the nature of the transformation and the quantity of the substance submitted to the transformation, on the heating rate and on the potential interferences determined by other substances present as well.

In parallel to the thermogravimetric analysis, in the above-mentioned temperature range, differential thermal analysis is performed (DTA) by a Perkin Elmer thermoanalyzer TG S-2 and DTA 1700.

Major operational condition for obtaining quantitative results - as long as the concentrations of the substances under consideration are significant and no simultaneous transformation or interferences occur - is the heating rate, currently used as 10°C/min.

However, in order to save time, at least at the preliminary stage of the DTA analyses, a rate of 20°C/min is used. The DTA curves, not published here, provide information about the endothermic or exothermic character of the temperature peaks. Hence, the results of DTG which were obtained properly at lower rates, were directly used for a quantitative analysis.

The analyses of the crystaline phases are performed by a Siemens D-500, X-ray diffractometer (with a monochromator of grafite crystal and an anticathode of Cu) based on an automatic adjustment and analysis system, aided by a Diffract-EVA quality analysis software. Typical measurement conditions to facilitate direct confrontation of various spectra, provide a diffraction interval between 2θ-5 and 2θ-60, with a step of 0.02.

Results and discussion

The curve of granulometric distribution and the curves presenting the distribution of the CO2 content (%) as well as hydraulic water % in function with granulometric fraction dimensions are given in the figures 1, 2 and 3, which indicate the following:

- the fractions in the 0-63μm range (figure 1) do comprise the binding material, corresponding to an almost 35% of the total, for the 1.1 sample, 20% for the W1 and ~12% for the 2.1 and 3.1.
- in general, the fractions between 63-2000μm, which correspond to the aggregates, follow more or less the same trends in all of the samples, varying per fraction around 5-10% of the total, which diversifies, the 2.1 and 3.1 from the W1 and 1.1.

In the fraction representing the binding material all the samples present the same CO2 content (figure 2), around the ~25%, as well as hydraulic water (figure 3) around the ~6% which shows the same analogy (1:1) of hydraulic to lime binder.

The above derives from taking into consideration that 1% of hydraulic water, according to the cement chemistry, represents 3-4% of hydraulic binder.

However, in order to assume the binder / aggregate ratio per volume of the initial mixture the % of the fraction to the total has to be taken into consideration.

Hence the 2.1 and 3.1 mortar samples contain a combined binder at a ~27% of the total, the W1 at a ~30% of the total and the 1.1 at a ~40% of the total. The equivalent

binder / aggregate ratios which can be assumed are:1/3-4, 1/3 and 1/2.5 correspondingly.

The TG, DTG and XRD analysis results are shown in the Tables 2 and 3.

Table 2 : TG-DTG (weight loss per temperature) results

Mortar	weight loss per temperature range (oC)					Hydraul . water %	CO2 / Hyd.wat .	T CO2 (°C)
Samples	<120	120-200	200-400	400-600	> 650			
1.1	1.98	0.68	1.98	2.80	19.47	4.78	4.07	780
2.1	1.19	0.45	1.50	3.25	11.22	4.75	2.36	760
3.1	1.14	0.48	1.39	2.13	11.02	3.52	3.13	760
W1	2.28	1.38	1.99	3.19	14.00	5.18	2.70	760
1a matrix	0.72	0.96	1.44	2.87	12.69	4.31	2.94	790
1b matrix	1.14	0.57	0.57	3.22	11.18	3.79	2.95	770

Table 3 presents the weight loss % estimated from the TG-DTG curves within the temperature ranges selected to give important information. Moreover, table 2 exhibits the hydraulic water %, calculated in the temperature range 200-600°C, the ratio CO2/H2O bound to hydraulic components and the temperature of CO2 decomposition. Table 4 presents the data for the granulometric fractions used for the construction of the figures 2 and 3.

In figure 4, spectrum of thermal analysis results concerning ancient, byzantine, post byzantine and later historic mortars from Greece is presented and the relevant information concerning the characterization of the Hagia Sophia mortars are validated.

The DTG of the crushed brick mortars demonstrates a series of peaks indicating:

- weight loss (~1-2%) of absorved moisture water at about 80°C
- weight loss (over 3.5%) of water bound to the several calcium aluminum silicate hydrates (CSH, CACH, CAH, Tb) at about 200-260°C, 480-520-580°C, the latter when argillaceous compounds like montmorillonite or illite are traced.
- weight loss (ranging from 6-33%) of CO2 during the calcite decomposition between 760-820°C, depending on the clay content of the matrix.

In distinction, the modern cement plaster from Hagia Sophia shows the characteristic peaks of transformation concerning gypsum and adsorbed water (<120°C), CASH (520-600°C) and CaCO3 at 760°C.

XRD results show the presence of CSH, CSAH, CACH, Chl, Tb, Prt, Il. The TG curves present a weight loss due to:

- moisture water (1-4%) at about 80°C
- water (3-16%) bound to alluminum-silicates hydrates, presenting peaks at 280, 450, 480°C- when CASH or CACH is detected. These are characteristic peaks of the so called "pozzolanic" reactions.

The CaCO3 decomposition occurs at about 740-820°C. The weight loss of CO2 varies mainly between 10-20% indicating lime aggregate ratios around 1:3.

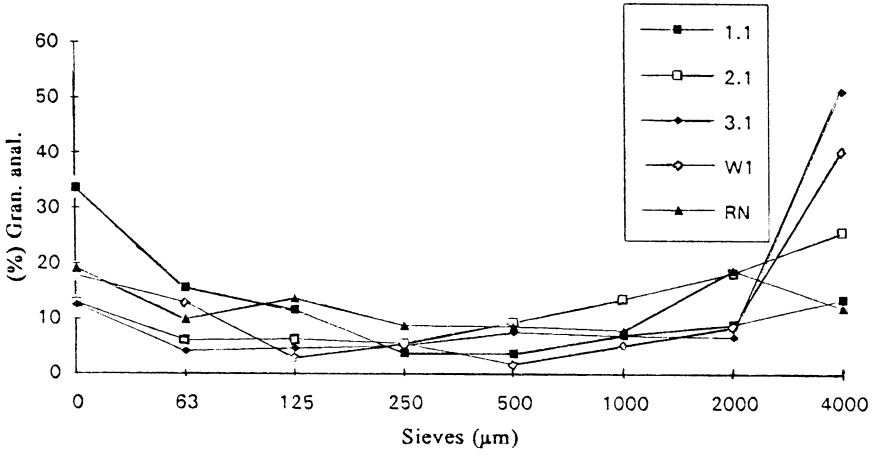


Fig. 1 Granulometric Distribution

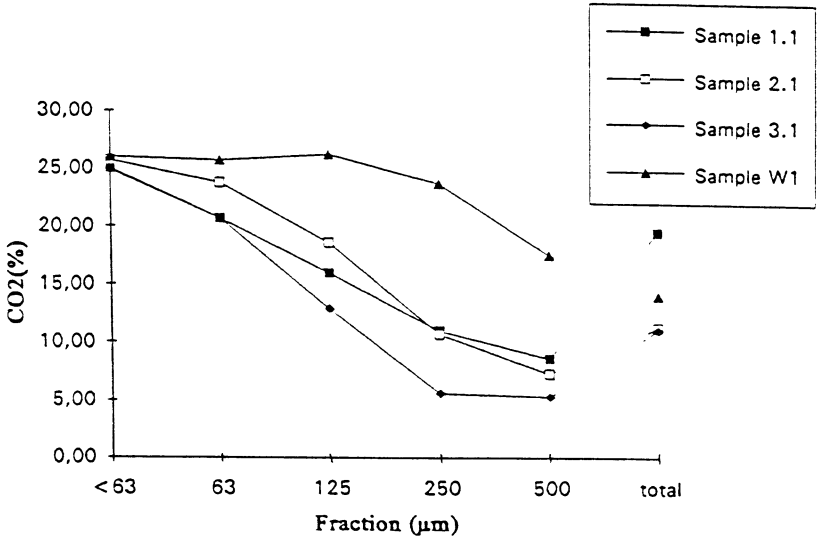


Fig. 2 CO2 content per granulometric fraction

Table 3: TG-DTG (weight loss per temperature) per fraction - results

	weight loss per temperature range ^{0}C						
	<120	120-200	200-400	400-600	>600	Hydraulic	CO2/hyd
Sample						water (%)	water
1.1 total	1,98	0,68	1,98	2,80	19,47	4,78	0,24
Fraction <63µm	1,55	0,69	2,37	4,04	25,01	6,41	0,26
" 63µm	1,35	0,60	2,06	3,12	20,66	5,18	0,25
" 125 µm	1,14	0,64	1,67	2,36	15,98	4,03	0,25
" 250 µm	1,09	0,78	1,63	2,48	10,96	4,11	0,38
" 500 µm	0,86	0,49	1,22	1,58	8,61	2,80	0,33
2.1 total	1,19	0,45	1,50	3,25	11,22	4,75	0,42
Fraction <63µm	1,65	0,67	2,90	3,39	25,73	6,29	0,24
" 63µm	1,16	0,68	2,24	3,00	23,77	5,24	0,22
" 125 µm	1,17	0,47	1,83	2,21	18,60	4,04	0,22
" 250 µm	0,97	0,39	1,55	1,55	10,69	3,10	0,29
" 500 µm	0,65	0,30	1,03	1,24	7,29	2,27	0,31
3.1 total	1,14	0,48	1,39	2,13	11,02	3,52	0,32
Fraction <63µm	1,64	0,86	2,60	3,68	24,88	6,28	0,25
" 63µm	1,37	0,83	2,24	3,14	20,66	5,38	0,26
" 125 µm	1,15	0,57	1,91	2,39	12,91	4,30	0,33
" 250 µm	0,93	0,36	1,07	1,31	5,60	2,38	0,43
" 500 µm	0,90	0,32	0,95	0,89	5,31	1,84	0,35
W.1 total	2,28	1,38	1,99	3,19	14,00	5,18	0,37
Fraction <63µm	3,17	2,13	2,69	2,98	26,00	5,67	0,22
" 63µm	2,70	1,80	2,25	2,71	25,70	4,96	0,19
" 125 µm	2,02	0,99	1,72	2,58	26,26	4,30	0,16
" 250 µm	2,41	1,00	1,81	2,41	23,71	4,22	0,18
" 500 µm	2,34	0,78	1,72	2,03	17,49	3,75	0,21

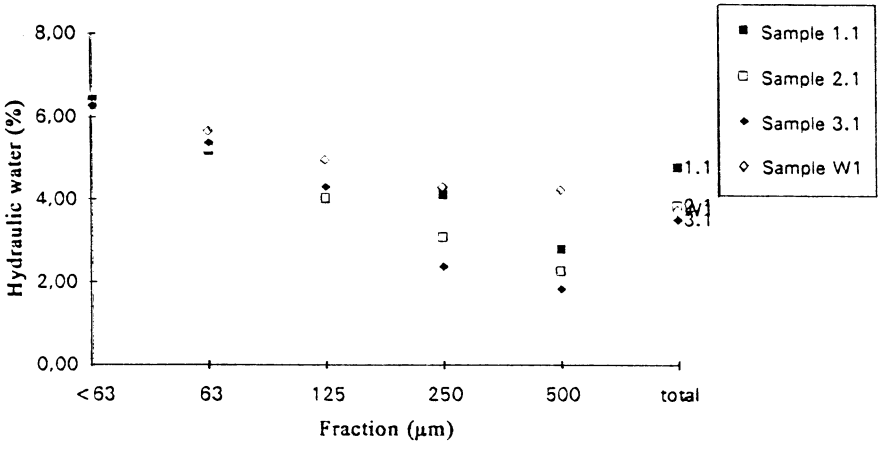


Figure 3 Hydraulic water per granulometric fraction

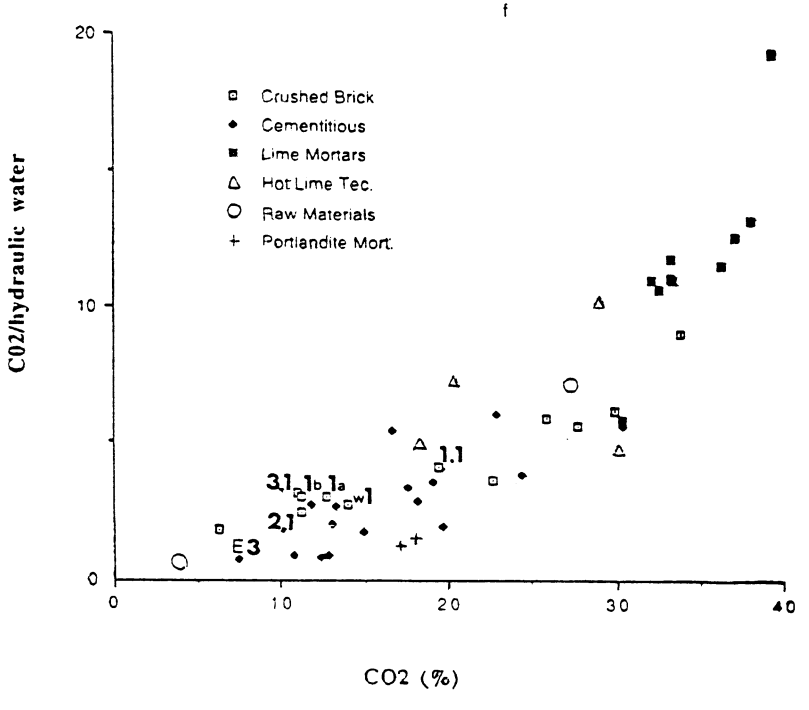


Figure 4 CO2/hydraulic water

Figure 4 presents the ratio of CO2/H2O bound to hydraulic components in function with the CO2 (weight loss %). The inverse trend of hydraulicity of the mortar samples is shown to augment exponentially with CO2. The cementitious mortars are concentrated at the bottom, the crushed brick and hot lime mortars in the middle of the curve and the typical lime mortars at the upper right of ratios >10% and CO2 >32%. The characteristics of crushed brick mortars fluctuated between 7.5-2.5 concerning the ratios and 10-33 concerning the CO2. In comparison with these generall limits, the Hagia Sophia mortar characteristics fluctuated between 4-2.5 and 10-20 correspondingly. Concequently, the Hagia Sophia mortars present more or less lower calcitic content and higher hydraulic one.

As shown in the figure 4, crushed brick-lime mortars of several technologies all over eastern Mediterranean Basin (11) present the binder / aggregates ratios between 1/4, 1/3 and 1/2.5, as determined for the Hagia Sophia mortars as well. According to Vitruvius "in using river or sea sand, the addition of a third part composed of burnt brick, pounded up and sifted, will make your mortar of a better composition to use". The same binder/aggregate ratio i.e. 1/3 has been found in the classical period crushed brick mortars in Greece (Rhodes, Nymphea Catacombs) and in the majority of byzantine mortars. In modern practice, a 1 to 3/5 volume ratio is preferred. However, the 1/4 ratios do not necessarily mean lime poor mortars produced on purpose. Most probably weathering physico-chemical phenomena, like dissolution, transport and recrystallization of salts, leading to salt decay, should occur, responsible for the washing out of calcite. Therefore, the 1/3 ratio could be selected as the proper mixture ratio to provide restoration mortars. This choice matches with the crushed brick mortar synthesis which was recently adopted in collaboration with Cretan monks to simulate byzantine technologies (10).

Conclusions

The above results account for a possible technology of a "pozzolanic" mortar, where one part per volume lime (in the analogy of 1/1 hydraulic to calcitic lime) was mixed with 3 parts of aggregates- the one to three being crushed brick fragments, the other one sea sand, and the third one most probably fine pozzolanic sand. However, up to now, analytical techniques cannot provide directly technology information, let alone on the physicochemical interactions among the constituents of historic walls, as in the case under study. Hence, a reverse engineering approach is needed to reveal traditional technologies for the production of restoration mortars (13), simulating byzantine technologies. Consequently, restoration mortars resembling the original ones should be provided instead of the modern cement mixtures.

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