ELSEVIER

Thermochimica Acta 321 (1998) 151–160

thermochimica acta

Characterization of structural byzantine mortars by thermogravimetric analysis

A. Bakolas[a,*], G. Biscontin[a], A. Moropoulou[b], E. Zendri[a]

[a] *Department of Environmental Sciences, University of Venice, 2137 Calle Larga S. Marta, 30123, Venice, Italy*
[b] *Department of Chemical Engineering, Section of Materials Science and Engineering, National Technical University of Athens, 9 Iroom Polytechniou, 15773, Athens, Greece*

Received 24 March 1997; accepted 17 May 1998

Abstract

The mortars and 'cocciopesto' plasters were largely used in the historic buildings, as waterproof coverings and in the preparation of mortars, especially in horizontal structures. In recent years, the necessity of restoration interventions with materials which are compatible with the masonry structure requires a detailed study on these materials. In this study, the composition of a significative number of mortars of the Byzantine period in the Hagia Sophia Basilica are investigated. They were made of 'cocciopesto' (crushed ceramic) and probably have a bearing function in the masonry structure. The samples are examined by particle size, infrared spectroscopy (FT-IR) and thermogravimetric analyses (TG-DTG), both on the total sample and on the finer fraction (<63 μm) which mostly constituted of binder. The results indicate slightly hydraulic mixtures made with a binder/aggregate ratio variable in volume between 1/2 and 1/4. The mixture morphology and heterogeneity seem to imply the use of hot lime technology that would lend themselves to the bearing function of the mortar. © 1998 Elsevier Science B.V.

Keywords: Mortars; Hydraulic compounds; Historic masonry; Lime-ceramic interaction; Particle size analysis; TG-DTG

1. Introduction

In the ancient Roman building, a particular type of mixture called 'cocciopesto' (crushed ceramic) was widely used as waterproof covering (for tanks, wells, and aqueducts) and, for the preparation of mortars, especially in horizontal structures. The cocciopesto mortars are composite materials, constituted of lime, ceramic fragments and/or ceramic powder, and other stone aggregates [1–3]. The nature of these materials is considered hydraulic, on the basis of possible interactions between the calcium hydrate and ceramic, probably forming calcium silico-aluminate hydrates. These kinds of interactions are usually called pozzolanic reactions, owing to the analogy of the interaction between natural pozzolana and hydrated lime [2,4].

There are various reasons that make a study on cocciopesto materials necessary: the wide use and importance they had in the ancient Roman, Byzantine and post-Byzantine building, and more generally in the traditional one; the lack of information about the composition and the production technology of these materials; the large desire, recently, of restoration materials that are compatible with the masonry structure [1,5].

---

[*] Corresponding author. Tel:. +39 41 2578509; fax: +30 41 2578584.

PII: S0040-6031(98)00454-7

The reconstruction of the original composition of the mixtures is often quite complex, owing both to the transformations that the components undergo during the time, and to the fact that the investigated systems can be disturbed differently in their single components. Therefore, the reconstruction of the original composition is often a rather arduous task, and anyway will require the results of various complementary techniques of investigation [5,6].

The analysis has to provide answers of a cognitive nature so as to identify raw materials, their relationship to each other, the dimensions of the aggregates, and to furthermore define the microstructure, identify the extraneous compounds and, if possible, the quality of the existing adhesive bond with the support.

Thanks to this characterization, it will be possible to prepare restoration mixtures having characteristics compatible with the masonry structure, through a 'reverse engineering' process [6].

The Great Church, Hagia Sophia of Constantinople (532–537 AD), is famous for its architectural and artistic magnificence and for the complexity of its restoration through the centuries. The first restoration work began very early, a little after its erection with the collapse of the Great Dome in the year 558 AD [2]. Current restoration efforts have to face a wider spectrum of problems and need a broader cooperation.

In this research the composition of a significant number of mortar joins of cocciopesto taken from the Basilica of Hagia Sophia is evaluated, by thermogravimetric and infrared analyses of the total sample and of the most representative particle size fractions.

2. Experimental

2.1. Sampling

According to historical data, the sample were taken from the joints of various masonries that date back to the Byzantine period, from the 6th to 10th centuries. They are representative of construction periods of different parts of the building. The joints of the brickwork structure are 5–7 cm thick, and probably have a bearing function. From a technological point of view they are similar to Roman concrete, because of the dimensions of the aggregates and of their consistency. The samples were taken from the upper parts of the building in order to avoid phenomena caused by the capillary rise.

Table 1
Sites of sampling

Sample	Site of sampling
AS1	Tambour, west side, outer face
AS2	Cornice level tunnel at the cornice entrance
AS3	Tambour, inner face
AS4	North main arch, inner face
AS5	Northeast exedrace dome, outer face, window level
AS6	Northwest buttress pier, west side, outer face
AS7	Southwest buttress pier, western inner wall
AS8	Southwest buttress pier, interior fill-south main arch
AS9	Main west arch, 9th mortar
AS10	Rib 16
AS11	10th mortar from left west main arch
AS12	West main arch, 25th mortar from left
AS13	24th mortar from right west main arch
AS14	Northwestern buttresses
AS15	North main Arch/west point
AS16	Southeastern abatement
W1	City walls

From the macroscopic point of view, some samples differ in color, dimensions, and in the consistency of the aggregates.

Table 1 reports the sampling sites of the investigated samples.

2.2. Analysis

The characterization of the mixtures was performed by the following procedures:

- Particle size analysis to assess the granulometry of the mixtures and to obtain information about single component. The mortar samples were fractionated and sieved through ISO 565 series sieves.
- Infrared spectroscopy (FT-IR, Biorad FTS 40) for the qualitative identification of the various compounds that are present in the mixtures.
- Thermogravimetric analysis (TG-DTG, Mettler TG 50) to determine quantitatively the various compounds in the total sample and in, the corresponding finer sieved fraction ($<63\,\mu m$), that is considered to mostly constitute the binder. The analyses were carried out at a range of temperature

Table 2
TG-DTG analysis of the total samples and CO_2/H_2O ratio (weight loss % >600°C/weight loss% between 200–600°C)

Sample	Weight loss in each temperature range (°C)				
	<120	120–200	200–600	>600	CO_2/H_2O
	(%)				
AS1	1.29	0.29	2.50	9.83	3.93
AS2	0.94	0.21	2.64	10.86	4.11
AS3	1.71	0.23	2.89	10.91	3.77
AS4	1.00	0.21	2.80	10.78	3.85
AS5	0.98	0.19	2.29	13.96	6.10
AS6	1.35	0.25	2.83	10.70	3.78
AS7	3.25	0.49	2.87	9.82	3.42
AS8	2.02	0.31	2.91	11.06	3.80
AS9	2.47	0.57	3.84	15.07	3.92
AS10	3.80	0.54	5.04	17.36	3.44
AS11	3.23	0.62	4.40	17.16	3.90
AS12	3.35	0.65	4.70	17.77	3.78
AS13	4.14	0.71	5.26	15.34	2.91
AS14	1.88	0.51	3.83	19.47	5.08
AS15	1.24	0.45	2.92	12.13	4.15
AS16	1.14	0.41	2.90	11.50	3.96
W1	2.28	1.02	3.66	15.52	4.24

30–1000°C with a heating rate of 10°C/min in a nitrogen atmosphere.

- Calcimetry (gas volumetric method) was used to determine CO_2 and to compare it with the results of TG.

2.3. Results and discussion

Table 2 shows the thermogravimetric analyses carried out on the total samples (Figs. 1–3), while Table 3 shows the results on the finer fractions (<63 μm) (Fig. 1(a), Fig. 2(a),Fig. 3(a)). The temperature ranges and the relative weight losses are as reliable for the characterization of these materials [3,6–8]. In particular, the temperature ranges correspond to the weight loss due to adsorbed water (<120°C), when there are not particular hydrated salts present, to the loss of chemically bound water (200–600°C), when there are no other compounds that undergo weight loss in this temperature range and to the loss of CO_2 (>600°C) due to the decomposition of carbonates.

The total sample data, carried out on a significant quantity in order to avoid errors caused by heterogeniety, shows that the CO_2 percentage was rather low, varying from 10% to 20%, thus indicating aggregates mostly of silicate nature. In most cases carbonates decompose below 600°C. This was confirmed by the determination of CO_2 by calcimetry. The decrease in decomposition temperature might be due either to the presence of compounds that favour decomposition, especially soluble salts, but also of other mineral compounds in the mortars, or to the dimension and defective state crystal lattice [6,7,9].

The percentage of CO_2 in the finer fractions (<63 μm), which mostly constituted of binder although only a small quantity of finer aggregate was present, had higher values. These were generally double than those of the total sample.

When the effective percentage of CO_2 (CO_2 binder) of the finer fraction in the total (by multiplying the percentage of CO_2 in this fraction by the weight factor of the fraction in relation to the total), was detected the values varied from 4% to 9%. Through this difference in percentage between the total CO_2 and CO_2 binder, the percentage of CO_2 effectively contained in the aggregate was obtained. This often exceeded the binder fraction. Such values varied from 3.5% to 14%; that could correspond to a $CaCO_3$ content of 8–32%.

The weight losses in the 200–600°C range may be attributed to the chemically bound water, and are indicative of hydraulic compound in the binder fraction. In this range there might also be losses of other compounds, such as calcium and magnesium hydroxide, hydromagnesite, organic compounds, etc. These were not noticed by infrared spectroscopy.

The weight losses of the total sample in the 200–600°C temperature range varied from 2.29% to 5.26%, whereas in the binder fraction the losses were higher, varying from 3.34% to 6.84%.

By calculating the percentage of binder H_2O, with the same procedure adopted for the binder CO_2, data revealed that the effective bound water of the finer fraction in the total sample varied from 1% to 2%. This was probably an indicator to the presence of a hydraulic portion in the mixture. These hydraulic compounds, probably calcium silico-aluminate hydrates, could be a result either of the lime/ceramic reaction, or of the employment of limes of marly nature. In any case, the content of hydraulic water is generally inferior to the 50% of the total water, which means that the aggregate contains a small amount of bound

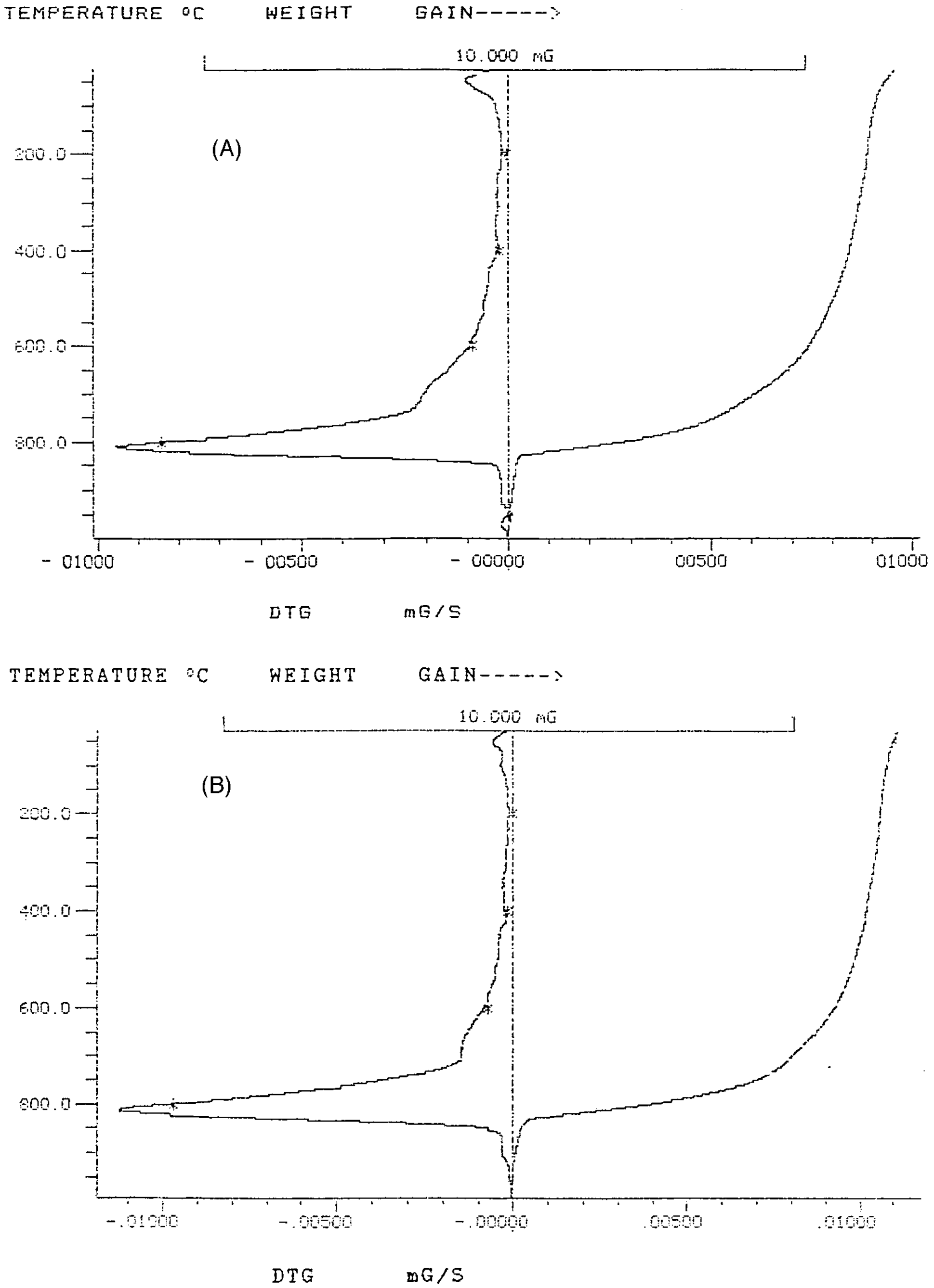

Fig. 1. TG-DTG plot of the total sample AS5. (a) TG-DTG plot of the finer particle size fraction of the sample AS5.

water, varying from 1% to 3%. Such water could be attributed to the rehydration of the ceramic, as this constitutes a great part of the aggregate probably baked at a low temperature, or from other processes that might have taken place during the long working-out of these mixtures, such as the clayforming process.

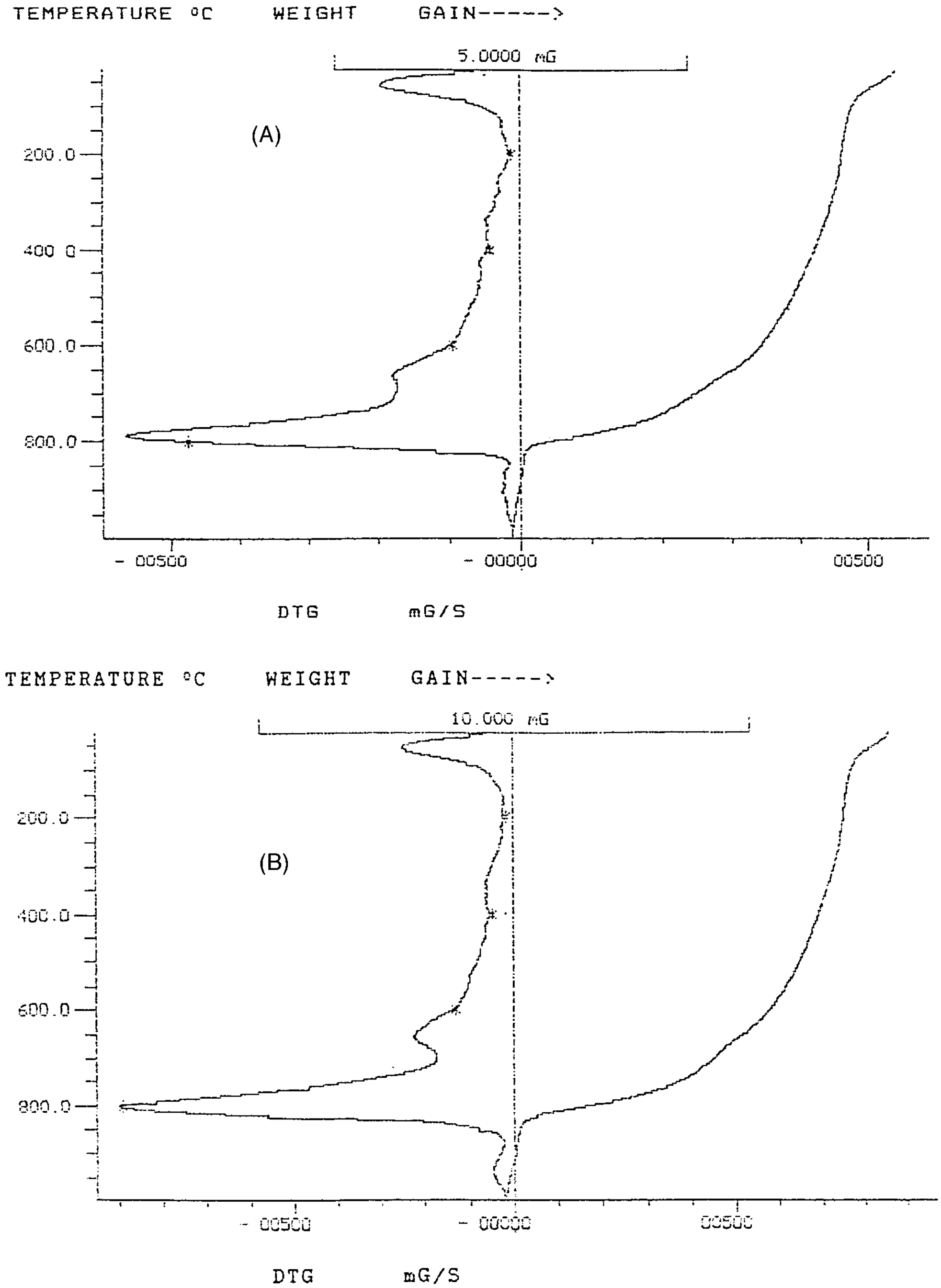

Fig. 2. TG-DTG plot of the total sample AS8. (a) TG-DTG plot of the finer particle size fraction of the sample AS8.

Part of this water could also result from the loss of constitutional water of minerals contained in the aggregate.

The CO_2/H_2O ratio between the weight loss percent ascribed to the CO_2 (>600°C) and the weight loss percent attributed to the hydraulic water (200–600°C)

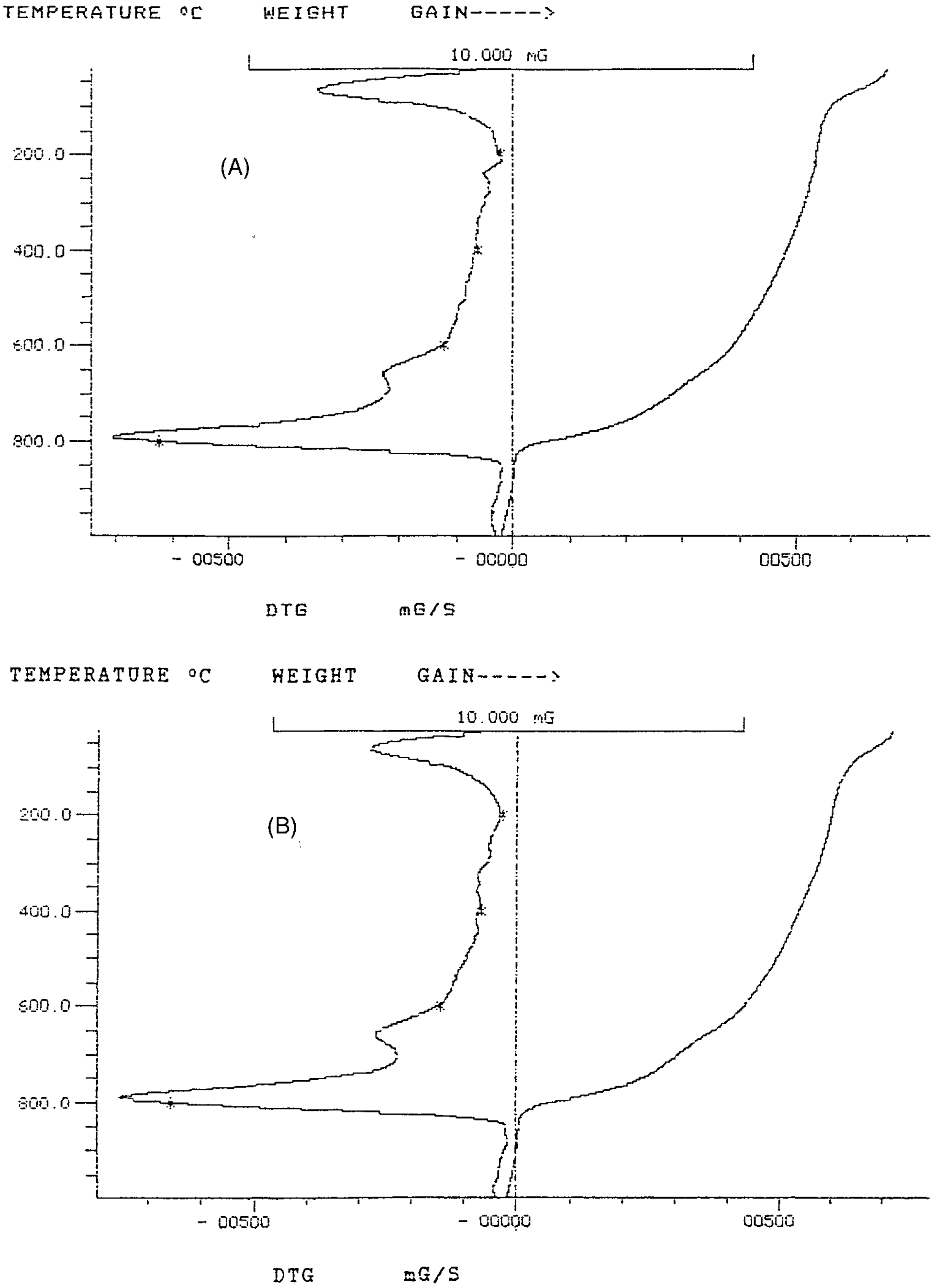

Fig. 3. TG-DTG plot of the total sample AS11. (a) TG-DTG plot of the finer particle size fraction of the sample AS11.

is of particular interest. This ratio that could give important indications on the hydraulic nature of a mixture in the total sample, is much more significant in the binder fraction [7,8]. Fig. 4, reports the values of percent hydraulic water vs. the CO_2/H_2O ratio referred to the binder fraction (<63 μm), shows an inverse

Table 3
TG-DTG analysis of the finer particle size fractions (<63 μm), CO_2/H_2O ratio, CO_2 binder percent, H_2O binder percent and weight percent of the particle size fraction <63 μm

Sample	Weight loss in each temperature range (%)				CO_2/H_2O	H_2O binder (%)	CO_2 binder (%)	Weight of the finer particle size fraction (%)
	<120	120–200	200–600	>600				
AS1	1.57	0.51	3.55	13.95	3.93	1.28	5.03	36.06
AS2	2.15	0.46	3.86	25.33	6.56	0.86	5.68	22.44
AS3	2.74	0.43	5.35	24.66	4.61	1.35	6.20	25.16
AS4	1.55	0.56	4.26	26.60	6.24	0.75	4.67	17.56
AS5	1.19	0.24	3.34	30.97	9.27	0.83	7.68	24.80
AS6	1.86	0.41	4.34	24.38	5.62	0.94	5.29	21.70
AS7	4.18	0.75	6.45	25.82	4.00	1.58	6.32	24.46
AS8	2.85	0.45	5.37	24.59	4.58	1.20	5.51	22.42
AS9	2.54	0.63	5.29	24.13	4.56	1.74	7.96	32.99
AS10	4.10	0.59	6.06	19.35	3.19	1.17	3.75	19.36
AS11	4.01	0.87	6.72	21.79	3.24	2.22	7.19	33.01
AS12	4.26	0.50	6.45	25.31	3.92	1.53	5.99	23.67
AS13	4.47	0.94	6.84	22.50	3.29	2.31	7.61	33.84
AS14	2.38	0.43	5.16	26.25	5.09	1.74	8.83	33.65
AS15	2.25	0.67	5.35	25.90	4.84	0.98	4.76	18.39
AS16	2.27	0.86	5.19	25.99	5.01	0.96	4.83	18.57
W1	3.32	1.42	5.21	26.82	5.15	1.09	5.60	20.89

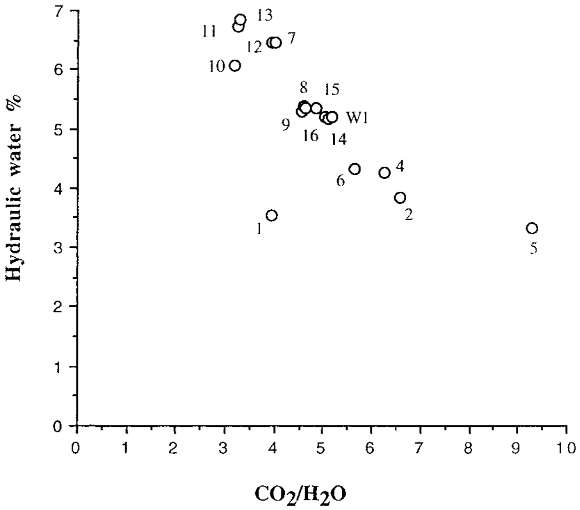

Fig. 4. Hydraulic water percent vs. CO_2/H_2O ratio (weight loss percent >600°C/weight loss percent between 200-600°C) referred to the finer fraction (<63 μm).

relationship between them. In fact, the highest bound water values corresponded to the lowest values ratios whereas the lowest hydraulic water values corresponded to the highest ratio values. In Fig. 4, three distinctive groups were observed: the first having values of hydraulic water >5.5% and $CO_2/H_2O<4$ (Fig. 3(a)), the second having values of hydraulic water <4.5% and $CO_2/H_2O>5.5$ (Fig. 1(a)), and the third having intermediate values (Fig. 2(a)).

Taking into account that a small percentage of the aggregate is included in the binder fraction (<63 μm) as observed by the optical microscopy and from the percentages of CO_2 and H_2O binder, the binder/aggregate ratio result from 1/2 to 1/4 in volume. This ratio indicates various preparation technologies employed for the production of the mixtures.

The weight loss in the 120–200°C temperature range, attributed to the crystallization water of hydrated salt, was less than 1% both in the total sample and in the binder fraction. Only a sample, taken from the city walls, exceeded the content of 1%, which was attributed to the loss of crystallization water of the gypsum that was identified by infrared spectroscopy (Fig. 5). Such gypsum quantity is more likely to be related to the sulphation of the carbonate component, or to the accumulation of soluble salts in the masonry rich in sulphates. The presence of gypsum seems to be improbable as binder for the relatively low concentration for such type of application.

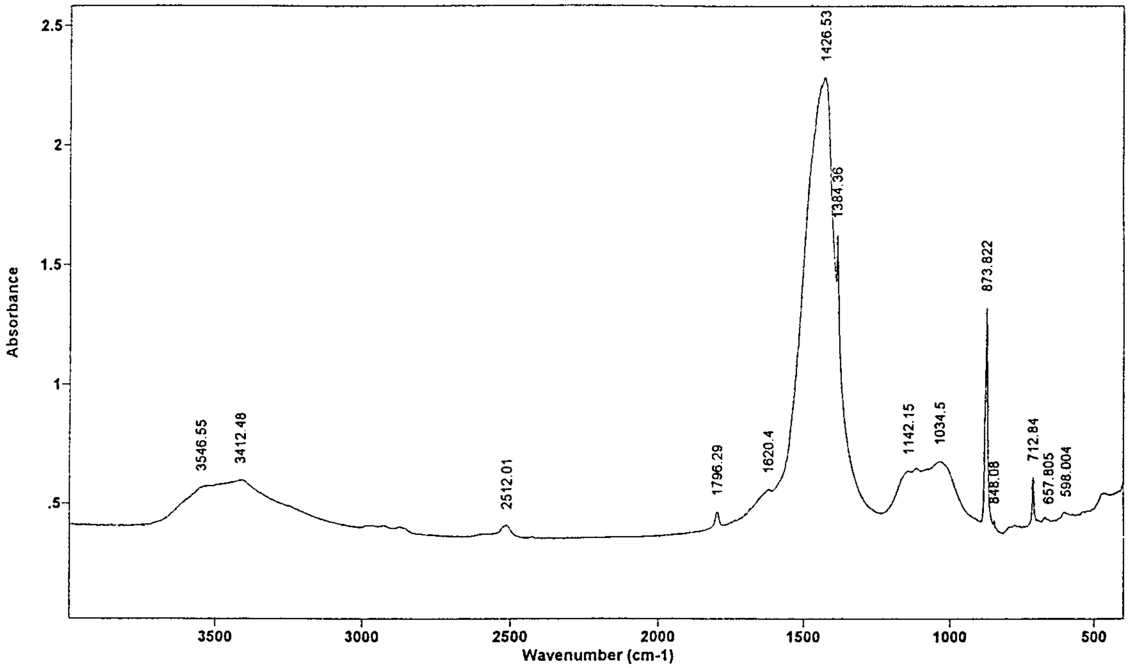

Fig. 5. Infrared spectrum of the total sample W1.

The weight loss in the temperature range <120°C, attributed to adsorbed water higher than 1%, both in the total sample and in the binder fraction, whose values were higher than those of the total sample. These values indicate mixtures of hydraulic nature that are hygroscopic materials, a property that turns out to be very useful in distinguishing hydraulic mortars from typical lime ones, as they usually have low contents of adsorbed water. Fig. 6 refers to the finer fraction, and shows the hydraulic water percent vs. the adsorbed water percent, we note there is a direct relationship between them.

Table 4 reports the results of the thermogravimetric analyses, carried out on the total sample and some granulometric fractions, and the corresponding weight percentage of each particle size fraction. The weight losses decreased as the granulometric fraction diameter increased, and in general their effective content in relation to the total sample (by multiplying the percentage of weight loss in each temperature range by the weight factor of each sieved fraction in relation to the total).

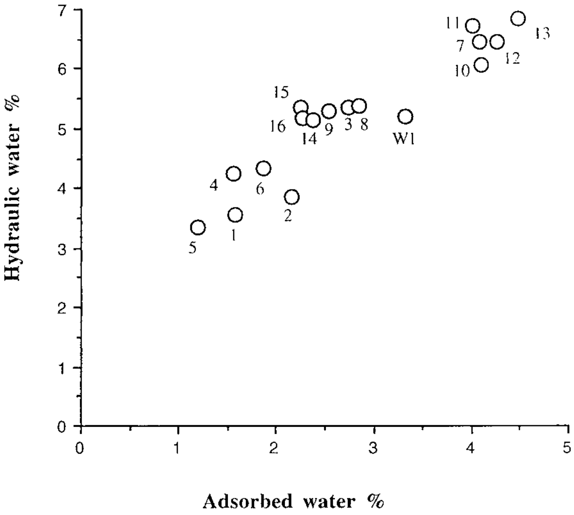

Fig. 6. Hydraulic water percent (weight loss between 200-600°C) vs. the adsorbed water percent (weight loss <120°C) referred to the finer fraction (<63 μm).

The percentage content of CO_2 in these fractions should be put in relation with the lime penetration into the ceramic structure, with the raw materials used for the production of the ceramic, and with the temperature at which it was baked. Finally part of the CO_2 could derive from the carbonation process of the

Table 4
TG-DTG analysis of the total sample and some particle size fractions

Sample	Weight loss (%) in each temperature range (°C)				Weight of the particle size fraction (%)
	<120	120–200	200–600	>600	
AS14 Total	1.88	0.51	3.83	19.47	
Particle size <63 μm	2.38	0.43	5.16	26.25	33.65
>63-<125	1.35	0.35	4.44	21.29	15.62
>125-<250	1.14	0.42	3.48	16.42	11.63
>250-<500	1.13	0.33	3.38	11.76	3.76
>500-<1000	0.98	0.33	2.45	8.83	3.65
AS15 Total	1.24	0.45	2.92	12.13	
Particle size <63 μm	2.25	0.67	25.35	25.90	18.39
>63-<125	1.28	0.40	4.81	23.24	6.03
>125-<250	1.26	0.31	3.47	18.60	6.34
>250-<500	0.97	0.29	3.02	10.52	5.57
>500-<1000	0.65	0.27	2.03	7.17	9.38
AS16 Total	1.14	0.41	2.90	11.50	
Particle size <63 μm	2.27	0.86	5.19	25.99	18.57
>63-<125	1.64	0.54	5.05	20.92	4.08
>125-<250	1.24	0.36	3.22	13.35	4.65
>250-<500	0.93	0.24	2.15	5.60	5.12
>500-<1000	0.90	0.22	1.84	5.19	7.54
W1 Total	2.28	1.02	3.66	15.52	
Particle size <63 μm	3.32	1.42	5.21	26.82	20.89
>63-<125	2.71	1.35	4.51	26.30	9.96
>125-<250	2.16	0.86	4.30	26.26	2.90
>250-<500	2.41	0.80	4.22	23.71	5.50
>500-<1000	2.34	0.78	3.75	17.49	1.72

calcium silico-aluminate hydrates contained in the hardened mortar, that react slowly with CO_2, thus forming $CaCO_3$, whereas silica and alumina separate in amorphous state [10]. The constitutional water could derive from the lime/ceramic interaction, which is much favoured if the baking temperature was about to 700–750°C with raw materials of kaolinite-montmorillonite composition [4]. Moreover, as was mentioned above, another percentage rate could be derived from the rehydration of clays and other minerals, contained in the aggregate.

3. Conclusions

All of the results obtained lead to the following conclusions on these traditional materials:

- the investigated mortars show different production technologies, having binder/aggregate ratios varying from 1/2 to 1/4 in volume. These ratios are similar to binder/aggregate ratios used in other historical periods.
- the employed binders present a slightly hydraulic character due to the use of raw carbonate materials of marly nature for the lime production, whereas part of the hydraulic compounds could derive from the lime/ceramic fragments interaction, or from the lime/ceramic powder interaction in case ceramic power was employed. The dimension of the ceramic fragments affects directly the hydraulic reactivity, but also the physico-mechanical behaviour in terms of porosity, transpirability, lightness and adhesion.
- the reactivity of the ceramic surface depends both on the composition of clays and on the baking temperature and conditions. The formation of hydraulic compounds in the interface is of difficult evaluation, owing both to their physico-chemical

condition and to the thickness of the involved material. Even taking into consideration a model of hydraulic type with formation of colloidal products, the analyses provide indications still in need of further confirmation by different techniques of investigation.

- the mixture morphology and heterogeneity lead to assume that hot lime technology was employed, as they would lend themselves to the bearing function of the mortar.
- the longevity of these materials could be attributed both to the chemical characteristics of the mixture, and to the microstructure and compatibility properties of the system that results from the combination of raw materials and preparation technology.

Acknowledgements

This research has been conducted thanks to the NTU-A, Bogazici University, Princeton University agreement for the Hagia Sophia earthquake protection. This research has been financially supported by the Italian National Research Council (CNR).

References

[1] R. Bugini, G. Capannesi, C.D' Agostini, C.F. Giuliani, A. Salvatori, A.F. Sedda, in M.J. Thiel (Ed.), Conservation of Stone and other Materials, Proc. Int. Cong. Rilem/Unesco, Paris, 1993, vol. 1, pp. 386–393.

[2] R.A. Livingston, P.E. Stuzman, R. Mark and M. Erdik, In: P.B. Vandiver, J.R. Druzik, G.S. Wheeler, I.C. Freestone (Eds), Materials Isssues in Art and Archaeology III, Mat. Res. Soc. Proc., vol. 267, Pittsburgh, PA, 1992, pp. 721–736.

[3] G. Biscontin, A. Bakolas, E. Zendri, D. Zancanaro, in Dal sito archeologico all'archeologia del costruito, Proc. Scienza e Beni Culturali XII, Bressanone, 1996, pp. 613–623.

[4] M. Giua, Trattato di Chimica Industriale, vol. 3, Utet, Torino, 1958.

[5] A. Bakolas, G. Biscontin, A. Moropoulou, E. Zendri, in: C.A. Brebbia, B. Leftheris (Eds), Structural Studies of Historical Buildings IV, vol. 1, Computational Mechanics Publications, Southampton, 1995, pp. 187–194.

[6] G. Chiari, M.L. Santarelli, G. Torraca, Materiali e Srutture 3, (1992) 111–137.

[7] A. Bakolas, G. Biscontin, V. Contardi, E. Franceschi, A. Moropoulou, D. Palazzi, E. Zendri, Thermochim. Acta, 269/270 (1995) 817–828.

[8] A. Moropoulou, A. Bakolas, K. Bisbikou, Thermochim. Acta, 269/270 (1995) 779–795.

[9] R.C. Mackenzie, Differential Thermal Analysis 1, Academic Press, London, 1st edn., 1970.

[10] C.J. Goodbrake, J.F. Young, R.L. Berger, J. Am. Cer. Soc. 62 (1979) 488–491.