



ELSEVIER

Thermochimica Acta 269/270 (1995) 817–828

thermochimica  
acta

## Thermoanalytical research on traditional mortars in Venice<sup>☆</sup>

A. Bakolas<sup>a,\*</sup>, G. Biscontin<sup>a</sup>, V. Contardi<sup>b</sup>, E. Franceschi<sup>c</sup>,  
A. Moropoulou<sup>d</sup>, D. Palazzi<sup>b</sup>, E. Zendri<sup>a</sup>

<sup>a</sup> *Dipartimento di Scienze Ambientali, Università di Venezia, 2137 Calle Larga S. Marta, 30123 Venezia, Italy*

<sup>b</sup> *Istituto di Chimica Generale, Università di Genova, 26 Corso Europa, 16132 Genova, Italy*

<sup>c</sup> *Istituto di Chimica Fisica, Università di Genova, 26 Corso Europa, 16132 Genova, Italy*

<sup>d</sup> *Department of Chemical Engineering, Section of Materials Science and Engineering,  
National Technical University of Athens, 9 Iroon Polytechniou, 15773 Athens, Greece*

Received 16 September 1994; accepted 9 June 1995

### Abstract

The study of traditional mortars has recently been attracting considerable attention, in connection with both diagnosis and applications required for restoration. The mortar is only apparently a simple system; in reality the lime is often accompanied by hydraulic components. The inerts often interact with the binder and the technologies used in the application are very diversified. These situations make the study of the mixtures rather complex, as it is difficult to distinguish the neoformation compounds from the older ones.

A basic approach is offered by granulometric analysis, allowing separation of the mortar into its components, in which the finer fraction is richer in binder. Some analyses on this fraction (< 63 μm) were performed to define the nature and quantity of the binder in the mortar. Samples were taken from various sites in Venice and were examined by calcimetry, TG–DTG and FTIR analysis. Moreover the investigation of this fraction by optical microscopy enabled us to distinguish the binder from the inert particles.

**Keywords:** Building restoration; Calcimetry; FTIR; Granulometric analysis; Mortar traditional; Optical microscopy; TG–DTG

\* Corresponding author.

<sup>☆</sup> Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September, 1994.

## 1. Introduction

The study of traditional mortars has recently been attracting considerable attention, in connection with both diagnosis and applications required for restoring. Reference literature discussing this subject is very sparse and quite heterogeneous both on the analytical–methodological approach and as to the understanding of the results. They are all hardly comparable with each other [1, 2]. In Venice, very little analytical research on mortars has been carried out. It deals with some historic buildings on which restoration has already been performed [3–5]. These studies offer specific indications for every individual situation, nevertheless, and do not comprise an evaluation of the problem as a whole.

For this reason systematic research on the historic mortars in Venice has been initiated. The aim is to identify the characteristics of the mixtures and evaluate the behaviour of these materials under the environmental conditions that prevail in the city [6]. Consequently, an analytical method has been set-up based on the chemical and physical characterization of the mortars and their most representative granulometric fractions. In particular infrared spectroscopy (FTIR) and thermogravimetric analysis (TG–DTG) were employed to characterize binders and inerts after granulometric separation. Infrared spectroscopy enables the detection both of the characteristic substances of the mortars (calcium carbonate, dolomite, silicates, calcium and magnesium hydroxides, gypsum, etc.), and the salts (nitrates, oxalates, sulphates, etc.). TG–DTG analysis determines quantitatively various compounds detected by the infrared spectroscopy [7].

The study of the mortars of Venetian buildings implies chemical characterization of the samples collected from buildings of various construction periods. Systematic analytical research along with historic research can contribute to the confirmation of the use of certain materials. It can also offer information about their behaviour. Also when comparing data derived from the various samples representative of different construction periods, it is possible to verify whether such materials were used deliberately and what technologies were employed.

From classic treatises, the use, in Venice, of lime with sand inerts was noticeable. This sand was collected in some cases from the Venice lagoon and was previously washed. The use of “cocciopesto” in the mixtures was another well known feature. In the treatises the use of lime has been mentioned even that called “calce nigra”, probably of hydraulic nature, deriving from the Euganei hills [8, 9].

In this specific research, the composition of a significant number of mortars was evaluated by thermogravimetric analyses of the mixture as a whole and the most representative granulometric fractions [10].

## 2. Experimental

### 2.1. Sampling

The samples were collected from 21 different sites in the city, from historic buildings constructed between the 14th and 18th centuries. During the sampling considerable

attention was paid to the phenomenon of capillary rise, which quite often occurs in Venice. As a result the samples were collected from zones higher than two metres from ground level, because mortars are considered to be uninfluenced by this phenomenon at that level. Sampling has been performed on both outer and inner parts of the buildings. The samples were different from the macroscopic point of view (colour, texture, grain, etc.). Table 1 reports the sampling performed on the various sites.

## 2.2. Analysis

Infrared spectroscopy was previously employed for the qualitative identification of the various compounds that are present in the mixtures (FTIR, Biorad FTS 40). The thermogravimetric measurements (TG–DTG) have been performed with a Mettler thermobalance (TG 50) and with a temperature gradient of  $10^{\circ}\text{C min}^{-1}$  up to  $1000^{\circ}\text{C}$  in static air atmosphere.

In order to obtain information about single components and their granulometric distribution, the mortar samples were fractionated and sieved through ISO 565 series sieves. The most significant granulometric fraction, for the aim of this particular research, is that of  $< 63\ \mu\text{m}$  containing the binder; although more or less significant quantities of fine grain inert frequently, and particularly in Venice, could be present in this fraction [10]. Moreover calcimetry has been performed to determine the  $\text{CO}_2$  content (Dietrich Fruhling).

Table 1  
Sampling sites

Site	Century of construction	Symbol of sample
Palazzo Zorzi	XVI	A1, A2
Chiesa di Santa Margherita	XVII	B1
Battistero di San Pietro di Castello	XVI	C1, C2
Palazzo Manfrin Venier	XVIII	D1, D2
Chiesa di San Zaccaria	XVI	E1
Palazzo Badoer	XVIII	F1, F2, F3
Chiesa di Santa Elena	XV	G1
Magazzini del Megio	XV	H1, H2
Case Gherardi	XV	I1
Scuola Grande di San Marco	XVI	L1, L2
Scuola Vecchia della Misericordia	XVI	M1
Palazzo Businello	XVII	N1, N2
Chiesa di San Andrea	XV	O1
Chiesa di Santa Maria Maggiore	XVI	P1
Palazzo Priuli	XIV	Q1, Q2, Q3, Q4
Chiesa dei Carmini	XVI	R1
Murazzi Lido	XVIII	S1
Corderie del Arsenale	XVI	T1, T3, T4, T5, T6, T7
Palazzo Bembo	XVII	U1
Ex Chiesa della Carità	XV	V1
Palazzo Nani	XV	Z1, Z2

### 3. Results and discussion

Table 2 reports the thermogravimetric analyses carried out on the mortar as a whole (total sample), whereas Table 3 presents the results from the single finer fractions ( $< 63 \mu\text{m}$ ). The temperature ranges and the relative weight losses represent the most significant parameters of this research. In particular, the temperature ranges are

Table 2  
TG-DTG analysis of the mortars (total samples)

Sample	Weight loss per temperature range ( $^{\circ}\text{C}$ )/%				Ratio(D/C)
	30–120	120–200	200–600(C)	> 600(D)	
A1	3.1	0.6	4.7	31.0	6.5
A2	1.8	0.5	3.5	34.5	9.6
B1	1.9	0.6	3.7	30.9	8.4
C1	1.5	0.8	3.8	34.0	8.8
C2	1.1	1.7	5.3	31.6	5.9
D1	0.7	3.6	1.4	8.2	5.6
D2	1.3	0.7	3.9	34.5	8.7
E1	2.4	0.5	2.7	30.5	11.4
F1	1.6	0.5	4.0	27.0	6.7
F2	2.7	0.4	3.5	32.9	9.4
F3	2.3	0.5	5.1	28.3	5.5
G1	3.4	1.0	6.0	33.0	5.8
H1	3.9	0.8	4.2	31.5	6.2
H2	2.2	0.4	3.8	35.7	9.3
I1	0.9	0.4	2.0	34.4	17.0
L1	2.3	1.5	8.3	24.9	3.0
L2	1.4	1.6	4.0	24.3	6.0
M1	1.4	0.5	3.5	35.2	10.0
N1	2.8	0.5	3.6	34.7	9.4
N2	1.5	0.6	4.2	35.5	8.5
O1	3.2	0.6	9.5	17.8	1.9
P1	1.0	0.4	3.1	32.2	10.5
Q1	1.7	0.4	5.9	32.1	5.5
Q2	1.2	0.4	4.8	34.8	7.2
Q3	1.9	0.6	5.4	28.8	5.3
R1	1.4	0.8	3.3	31.3	9.2
S1	2.1	2.7	5.7	10.3	1.8
T1	2.2	0.7	7.0	26.7	3.8
T3	1.7	0.9	5.1	30.4	6.0
T4	0.5	0.5	3.3	35.8	10.5
T5	1.1	0.4	3.0	34.9	11.5
T6	2.3	1.5	4.5	31.1	6.8
T7	2.4	1.5	5.1	28.7	5.6
U1	2.3	0.5	4.1	33.9	8.3
V1	1.8	0.5	3.8	31.4	8.3
Z1	2.0	1.0	4.5	30.5	6.8
Z2	3.1	0.9	6.9	23.6	3.4

Table 3  
TG-DTG analysis of the finer fractions (< 63  $\mu\text{m}$ )

Sample	Weight loss per temperature range ( $^{\circ}\text{C}$ )/%				Ratio (D)/(C)	Weight of finer fraction/%	Effective $\text{CO}_2$ /%
	30–120	120–200	200–600(C)	> 600(D)			
A1	3.0	1.4	6.6	29.6	4.5	35.1	10.4
A2	2.0	0.8	5.8	34.4	5.9	33.2	11.3
B1	2.6	0.5	5.0	29.2	5.8	39.1	11.4
C1	3.8	1.9	6.5	29.3	4.9	31.9	9.4
C2	3.4	3.0	7.6	24.7	4.5	37.5	9.1
D1	0.8	4.6	3.3	16.1	4.9	46.3	7.4
D2	4.0	0.8	4.9	37.8	7.8	37.1	14.0
E1	1.0	0.9	4.3	37.8	8.7	37.5	14.0
F1	2.8	1.1	6.0	25.9	4.3	45.2	11.7
F2	2.7	0.5	4.7	32.3	6.9	42.6	13.9
F3	4.5	1.1	6.5	32.3	4.9	46.7	15.1
G1	2.3	1.0	7.0	31.2	4.4	57.6	18.1
H1	2.6	2.8	6.2	29.3	4.6	38.0	11.1
H2	3.3	0.7	5.6	33.1	5.9	50.5	16.6
I1	4.4	0.9	5.6	29.8	5.6	13.3	3.9
L1	2.7	2.5	11.1	21.0	1.9	40.7	8.6
L2	1.8	3.9	8.1	20.4	2.6	29.4	5.9
M1	3.2	0.7	6.1	33.1	5.5	40.3	13.2
N1	2.7	0.7	6.1	34.4	5.7	44.1	15.4
N2	1.9	0.9	5.7	34.1	5.9	38.2	12.9
O1	6.2	1.7	13.6	13.1	0.9	33.8	4.4
P1	3.2	1.0	6.1	33.0	5.3	42.4	13.9
Q1	2.2	0.6	7.0	32.4	4.7	44.9	14.6
Q1	2.6	0.6	6.6	34.0	5.1	38.9	13.3
Q3	3.0	0.7	4.5	39.2	8.7	52.8	20.8
R1	2.7	0.5	5.2	31.5	6.2	47.3	14.8
S1	4.6	4.3	7.0	14.5	2.1	31.2	4.5
T1	3.4	1.6	10.8	23.9	2.2	49.1	11.7
T3	2.6	1.4	7.5	27.4	3.7	47.0	12.9
T4	0.9	0.7	5.0	38.1	7.6	42.3	16.0
T5	1.6	0.8	3.6	36.9	10.0	46.1	17.0
T6	2.2	3.1	5.4	27.3	5.0	41.9	11.5
T7	2.4	3.4	5.6	26.4	4.7	48.1	12.7
U1	1.5	2.8	5.1	29.9	6.0	42.5	12.6
V1	3.1	1.4	7.9	30.6	3.9	31.2	9.5
Z1	1.8	1.7	5.8	28.9	4.9	41.5	11.9
Z2	3.7	3.1	7.8	20.3	2.6	52.8	10.7

relative to the weight loss due to hygroscopic water (i.e physically adsorbed water < 120 $^{\circ}\text{C}$ ), to the loss of the water due to hydrated salts (120–200 $^{\circ}\text{C}$ ), to the loss of the water bound to hydraulic compounds (200–600 $^{\circ}\text{C}$ ) and to the loss of  $\text{CO}_2$  (> 600 $^{\circ}\text{C}$ ) [2, 11]. In various samples, a weight loss was detected in the temperature range 500–600 $^{\circ}\text{C}$ , followed by a weight loss attributed to the decomposition of carbonates.

The determination of the total CO<sub>2</sub> by calcimetry (gas volumetric method), confirmed that in some cases the weight loss in the temperature range 500–600°C is ascribable to the early decomposition of carbonates. In fact, it was noticed, but not fully clarified, that the presence of soluble salts in the mortar favours a decrease in the temperature at which the carbonates decompose [2]. However, the determination of the soluble salts revealed values between 5% and 10%. Tests on desalinated samples confirmed the above hypothesis, better illustrated in Fig. 1, which refers to the sample P1 before and after extraction of the soluble salts. A shifting of the peak relative to the CO<sub>2</sub> decomposition was detected.

The data shown in Tables 2 and 3 lead to the following remarks: the presence of considerable quantities of CO<sub>2</sub> is accompanied by high quantities of carbonates. These values indicate that a portion of the inert is carbonatic, as was expected because of the nature of the local sands employed [12]. Some of the samples have recorded a relatively low CO<sub>2</sub> content particularly those of the finer fraction, in contrast to the high CO<sub>2</sub> content of the total sample (usually between 24% and 36%). Samples D1 and S1 present a very low CO<sub>2</sub> content, both in the total sample and in the finer fraction, but record also a weight loss higher than the general trend in the temperature range 120–200°C corresponding to loss of water from the hydrated salts. In fact, this low quantity of CO<sub>2</sub> could be attributed in part to the gypsum binder. This hypothesis was confirmed by infrared spectroscopy (FTIR). In the temperature range 200–600°C a weight loss that could be attributed to the chemically bound water was detected, indicative of the presence of the hydraulic compounds, except that resulting from the occurrence of organic compounds. The values for the mortars and the finer fraction respectively, in this temperature range, are relatively high and vary for the total samples, by about 5–6%, despite some samples reaching 7–8% (with a maximum of 9.5% for sample O1). It is interesting to note that sample O1 presents a substantial weight loss at temperatures below 120°C. The above results are reported in Table 2.

The difference between the weight loss of the total samples and the weight loss of the finer fractions (< 63 μm), in the temperature range 200–600°C, reveals positive values, in general between 1% and 2%. This difference could probably indicate the presence of hydraulic compounds in the mixture. Fig. 2 shows the weight loss %, in the temperature range 200–600°C of both total samples and the finer granulometric fractions (< 63 μm) multiplied by the % weight of the granulometric fraction. These values are concentrated in a rather small area, where the water relating to the binder (fraction < 63 μm) is about 50 and 70% of the water in the total samples. Fig. 3 shows the values of the ratio (indicated as D/C) between the weight loss % (D) ascribed to the CO<sub>2</sub> (> 600°C) and the weight loss % (C) attributed to the hydraulic water (200–600°C) versus (D) referred to the total sample. Fig. 4 shows the values of the ratio (indicated as D/C) between the weight loss % (D) ascribed to the CO<sub>2</sub> (> 600°C) and the weight loss % (C) attributed to the hydraulic water (200–600°C) versus (D) referred to the finer granulometric fraction (< 63 μm). It should be noted that these figures describe only the corresponding ratios between the carbonatic fraction and the hydraulic ones, for the various samples.

Two areas can be noticed in Fig. 3: the first comprises values of CO<sub>2</sub> around 30% and with a D/C ratio between 5 and 7. The second one comprises values of CO<sub>2</sub> over

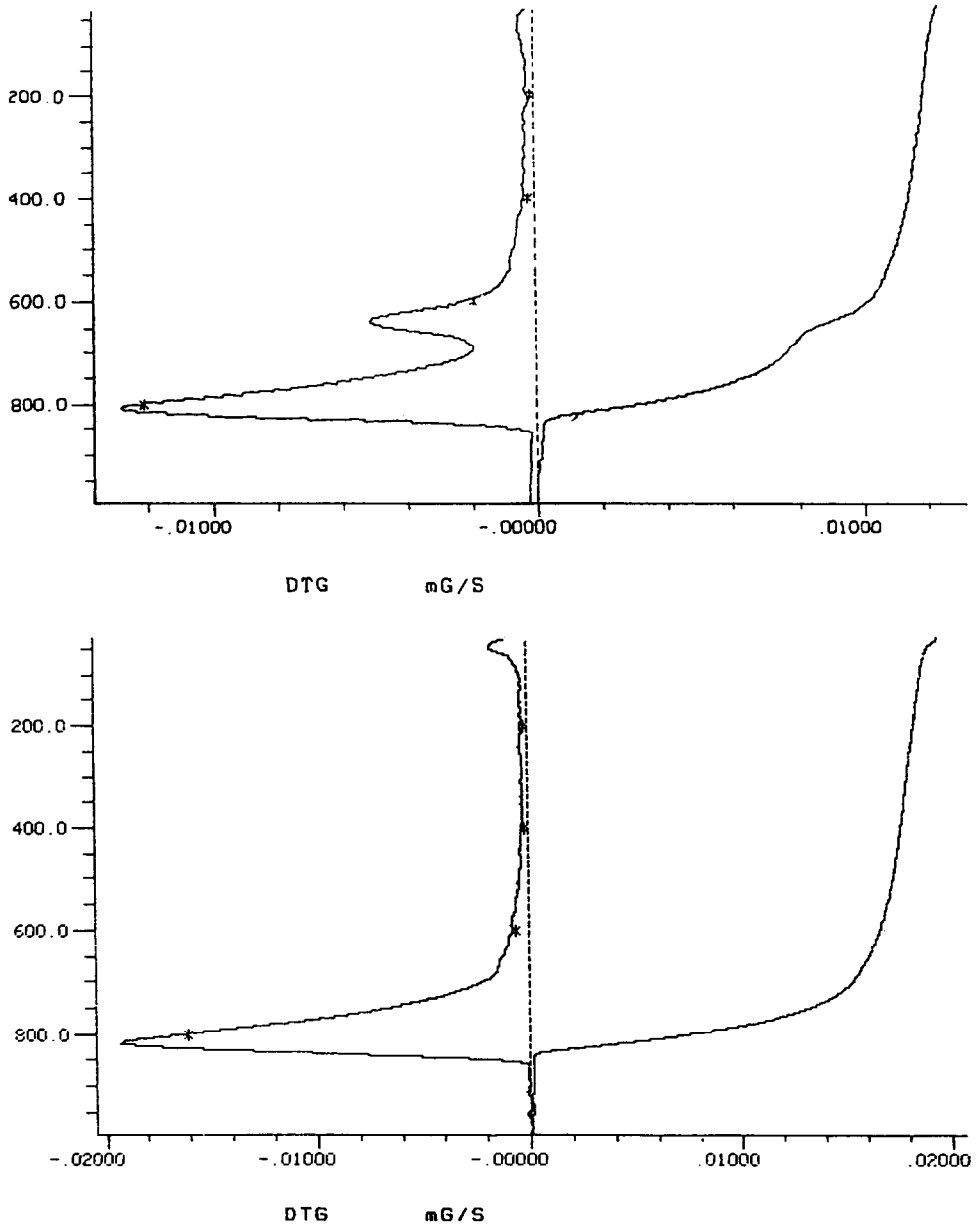


Fig. 1. TG-DTG analysis of the total sample P1 before (a) and after (b) desalination.

30%, with D/C ratio between 11 and 17. Nevertheless, there are cases that correspond to both low values of the D/C ratio (between 2 and 3) and very low values for  $\text{CO}_2$  content, indicating the presence of hydraulic compounds. In contrast, high values of the  $\text{CO}_2$ /hydraulic water ratio (D/C), could indicate the reduced presence of a hydraulic

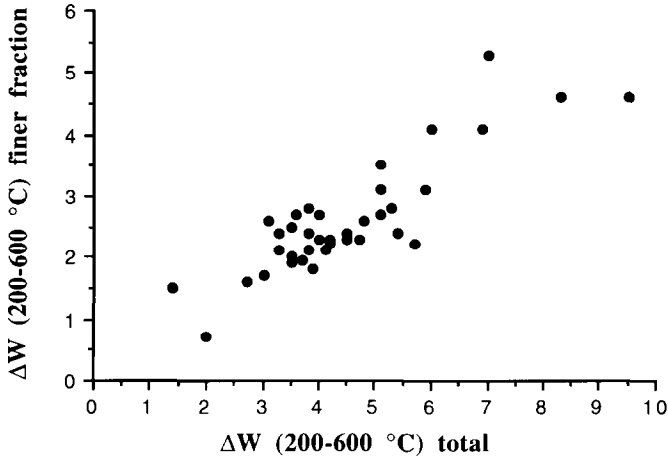


Fig. 2. Weight loss % in the temperature range 200–600°C of the total sample versus the weight loss % of the finer fraction multiplied by the % weight of the granulometric fraction (< 63 μm).

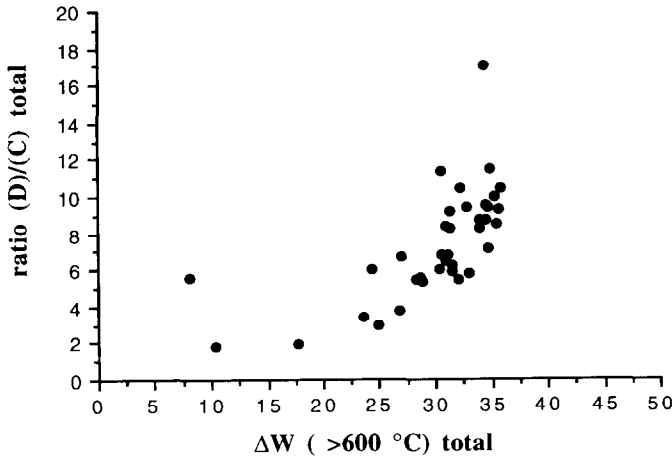


Fig. 3. (D/C) ratio between the weight loss % in the temperature range > 600°C (D) and the weight loss % in the temperature range 200–600°C (C) versus (D) referring to the total sample.

binder, even though the CO<sub>2</sub> content includes a part of inert and consequently could not be very representative.

In Fig. 4, the (D/C) ratio is reported versus the CO<sub>2</sub> content referred to the finer fraction. A group of fractions with a D/C ratio between 1 and 3 can be observed, corresponding to low values of CO<sub>2</sub> content (< 25%), a group with a D/C ratio higher than 7.5 with CO<sub>2</sub> content of around 38% and a group with intermediate D/C ratio and



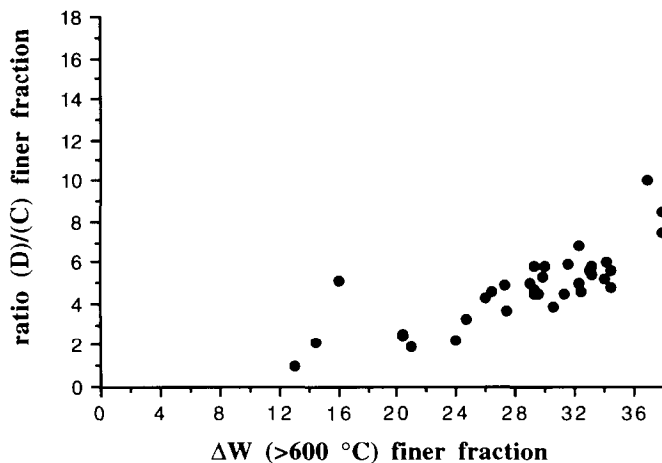


Fig. 4. (D/C) ratio between the weight loss % in the temperature range  $> 600^\circ\text{C}$  (D) and the weight loss % in the temperature range of  $200\text{--}600^\circ\text{C}$  (C) versus (D), referring to the finer fraction ( $< 63\ \mu\text{m}$ ).

$\text{CO}_2$  content. This could indicate that in the binder fraction ( $< 63\ \mu\text{m}$ ) a certain percentage of the inert is present and that part of the binder is hydraulic. The fractions with D/C values higher than 7.5 are indicative of an aerial binder, whereas those with D/C ratios lower than 3 and  $\text{CO}_2$  content lower than 25%, correspond to a binder constituted by a mixture with a substantial hydraulic fraction. The fractions with intermediate D/C ratio and  $\text{CO}_2$  content are indicative of an aerial binder with low hydraulic fractions.

From the percentage of the finer granulometric fraction ( $< 63\ \mu\text{m}$ ) it is possible to calculate the effective  $\text{CO}_2$  content (Table 3). The values calculated in this way, refer to the weight loss % of the finer fraction in the temperature range  $> 600^\circ\text{C}$  and, when multiplied by the percentage weight of the finer granulometric fraction, indicate that  $\text{CO}_2$  is present at about 12–15%.

Fig. 5 reports the  $\text{CO}_2$  values of the total samples versus those of the respective finer granulometric fraction, multiplied by the percentage weight of the granulometric fraction. Taking into account that a small percentage of the inert (around 2–3%) of carbonatic nature is included in the granulometric fraction  $< 63\ \mu\text{m}$ , as observed by optical microscopy, the binder/inert ratio is about 1:3. This ratio indicates that the proportion of binder/inert as well as the granulometric distribution of the aggregates were well defined during the traditional production of the mixture.

Fig. 6 presents the weight losses of the total sample in the temperature range  $< 200^\circ\text{C}$  versus the weight losses in the temperature range  $200\text{--}600^\circ\text{C}$ . Fig. 7 shows the weight losses in the above mentioned temperature ranges relative to the finer granulometric fractions. In Fig. 6 the majority of the samples in the temperature range  $< 200^\circ\text{C}$ , are concentrated in an area with a weight loss of 2–3%. In the area with weight losses over 3% one can find the samples that contain gypsum or hydraulic

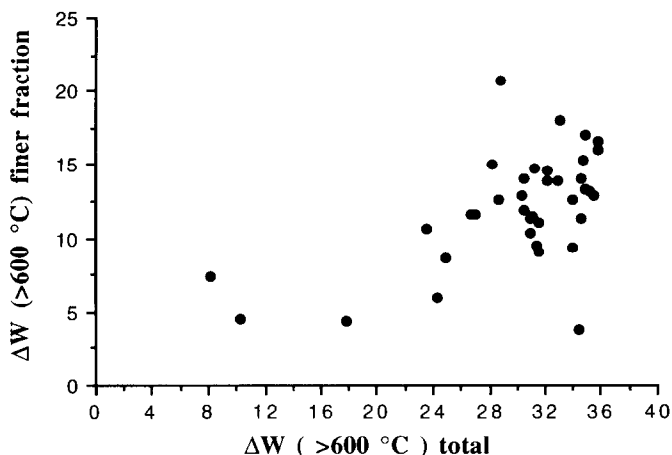


Fig. 5. CO<sub>2</sub> values as % of the total sample versus the respective CO<sub>2</sub> values as % of the finer fraction (< 63 μm) multiplied by the % weight of the granulometric fraction.

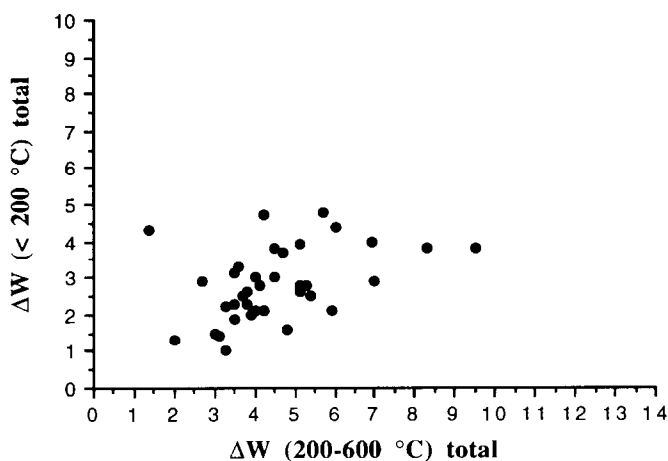


Fig. 6. Weight loss % in the temperature range 200–600°C versus the weight loss % in the temperature range 30–200°C referring to the total sample.

compounds, whereas in the temperature range 200–600°C, the weight loss % varies between 3–5.5%, in the area where the majority of the samples are concentrated. In Fig. 7 the values are located in a much broader area than that of Fig. 6 relative to the total samples. Thus the water bound to hydraulic compounds in the temperature range 200–600°C varies mainly between 4 and 8%, whereas at temperatures < 200°C the same values range from 2 to 6%.

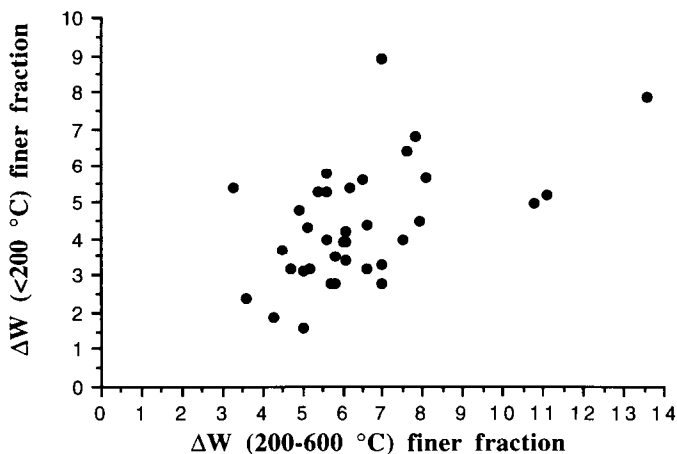


Fig. 7. Weight loss % in the temperature range 200–600°C versus the weight % loss in the temperature range of 30–200°C referring to the finer fraction (< 63  $\mu\text{m}$ ).

### 3. Conclusions

The results confirmed that the mortars were homogeneous, and that the ratio between binder and aggregate in the various samples was not random but, on the contrary, well defined. The hydraulic characteristics of the binder, are confirmed by the weight loss in the temperature range 200–600°C, both in the total samples and in the finer fractions. Nevertheless, the presence of the hydraulic compounds in the mixture should be further confirmed through other quantitative methods. The aggregates, as one could expect from the nature of the local sands, are prevalently carbonatic.

The results of the analyses cannot imply a relationship between the construction period and the preparation technologies of the mortars. In general, the mixtures present similar characteristics, especially in the proportions of binder and aggregate, which ever found to be about 1:3.

One sample revealed the presence of a large quantity of gypsum that was evidently used as a binder along with the lime. Moreover, some samples were characterized by the use of the binders with high hydraulicity, a feature strengthening the assumption that the use of such products was deliberate.

Finally, the impact of the soluble salts on the early decomposition of the calcium carbonate was confirmed.

### Acknowledgement

This research has been financially supported by the Italian National Research council (CNR).

## References

- [1] G. Alessandrini, in G. Biscontin (Ed.) *L'intonaco: storia, cultura e tecnologia*, Proc. Scienza e Beni Culturali I, Bressanone, 1985, pp. 147–166.
- [2] G. Chiari, M.L. Santarelli and G. Torraca, *Materiali e Strutture*, 3 (1992) 111–137.
- [3] G. Biscontin, G. Riva and F. Zago, *Bolletino d'Arte*, supplemento, 5 (1983) 43–50.
- [4] Meneghini, Estratto dagli atti del Reale Istituto Veneto di Scienze Lettere ed Arti, Venezia, 1937, Tomo XCVI, pp. 119–126.
- [5] E. Armani, *Bolletino d'Arte*, supplemento, 1 (1984) 69–76.
- [6] G. Biscontin, A. Bakolas, P. Maravelaki and E. Zendri, in M.J. Thiel (Ed.), *Conservation of Stone and other Materials Proc. Int. Cong. Rilem/Unesco*, Paris, 1993, Vol. 1, pp. 178–185.
- [7] G. Chiari, M.L. Santarelli and G. Torraca, in G. Biscontin (Ed.), *Calcestruzzi antichi e moderni: storia cultura e tecnologia*, Proc. Scienza e Beni Culturali IX, Bressanone, 1993, pp. 275–286.
- [8] V. Fontana, in Comune di Venezia (Ed.) *II Mattone di Venezia*, Proc. Int. Cong., Venice, 1979 pp. 39–52.
- [9] A. Palladio, *I Quattro Libri dell' Architettura*, Venezia, 1570, libro I.
- [10] G. Biscontin, A. Bakolas, A. Moropoulou and E. Zendri, in V. Fassina, H. Ott, F. Zezza (Eds.), *The Conservation of Monuments in the Mediterranean Basin*, Proc. 3rd Int. Cong., Venice, 1994, pp. 405–410.
- [11] R.C. Mackenzie, in *Differential Thermal Analysis 1*, Academic Press, London, 1970.
- [12] P. Jobstraibizer and P. Malesani, *Mem. Soc. Geol. Ital.*, XII (1973) 411–452.