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PLASTERS AND MORTARS IN THE CENTRAL BUILDING OF THE UNIVERSITY OF PAVIA
Thermal and structural study

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Plasters and mortars taken from the walls of the ancient hospital 'San Matteo' of Pavia (Italy), were investigated with thermal and other techniques. From the data collected, two groups of materials were brought out: the first one, containing the plasters, is remarkably richer in calcite than the second group, formed by the mortars. These findings allow one to relate these groups to two historical periods: the middle of the XV century, and the end of the XVIII century. Some hypotheses may also be made on the compositions of the binding/inert fractions adopted in preparing these materials in the building yards of the two periods.

Keywords: *ancient building materials, mortars, plasters, thermal analysis, thermogravimetry*

Introduction

The ancient hospital 'San Matteo' of Pavia was built around the middle of the XV century upon will of the citizens and is located in the historical centre of the city.

A thorough description of the hospital foundation decided by Pope Nicolò V in his bulla in 1449 is reported in an important historical work by Adriano Peroni [1] in which several maps of the buildings both in their original form and after subsequent changes are illustrated. In that work a comparison between the criteria adopted in building this hospital and those assumed in the Florence and Milan hospitals is also presented and discussed.

After some minor restorations, the hospital was rebuilt in the second half of the XVIII century by the Austrian government, in connection with the development of the Faculty of Medicine of the University, its anatomical theatre and museum. The projects and the architectural works carried out under Austrian rule between 1770 and 1789, coordinated by Leopold Pollach, are presented in a recent historical paper by Luisa Erba, devoted to the different hospital arrangements in the last two centuries [2]. The main building of the hospital was dismissed in 1932, then used by the army and finally acquired by the University of Pavia in 1951. It hosts now some University departments of the Faculties of Political Sciences and Humanities.

In recent years, some technical works were undertaken by the University of Pavia in order to set-up and to update the fire safety equipments. In this occasion, it was made possible to take some samples of plasters and mortars from cuttings made in the walls.

In the framework of such interventions, the present paper aims at providing useful physico-chemical information on the composition and properties of the plasters and mortars used in these walls.

It is well known that the properties and resistance of plasters and mortars after suitable setting conditions are a consequence of chemical reactions between lime and other materials used in the preparation procedure [3]. The quantitative determination of calcite and gypsum by thermal analytical techniques may be considered as a method providing information on the original lime content used in the building yard [4], whereas the detection of other binding materials possibly employed, e.g. clays and pozzolanic binders with their reaction products, may require a deeper investigation. In order to gain a better understanding, an endeavour to compare some samples taken from historical walls with mixtures of the close mineral composition freshly prepared was also made.

A further aim of this paper is to confirm the assignment of different materials to different historical phases of the hospital construction, and to compare their properties to those of materials belonging to other buildings of the same historical periods.

Experimental

Samples

A list of the samples taken in the ancient walls of the cross buildings of the hospital is reported in Table 1.

An example of the works carried out in 2003 on the masonry of the site where the samples could be

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Table 1 List of the examined samples

Sample	Description
1U	Fragment of mortar
1A	Plaster on the surface
1B	Plaster on the surface
2A	Plaster on the surface
2B	Mortar
3B	Mortar
3C	Plaster on the surface
4A	Plaster on the surface
4B	Mortar
5B	Plaster on the surface
5C	Mortar
5D	Mortar

taken is shown in Fig. 1, where a picture of the North wall in the Magnolias Courtyard, from which sample 3 was extracted, is illustrated.

In order to obtain a better recognition of the sample components, the following standard materials were chosen: calcite, gypsum, kaolin and montmorillonite. They were kindly provided by the Department of Earth Sciences of the University of Pavia. Moreover, several samples of fine sand were also collected as reference material from the left beach of the Ticino river near Saint Lanfrancus. A specimen of commercial calcium hydroxide was also taken into account as a material for comparison.

For the sake of comparison, some compositions of ancient materials sampled on the walls were experimentally reproduced by combining in the proper ratios the available standard materials.

Fig. 1 The site from which the samples 3 were taken

Methods

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TG) measurements were performed by means of a 2960 SDT simultaneous analyser (TA Instruments). Finely ground samples (~ 50 mg) were introduced into alumina pans and run at 10°C min^{-1}, between room temperature and 1000°C, under nitrogen purge or static air. The instrument was calibrated both in temperature and enthalpy with standard indium. A baseline correction was performed on each DSC curve by subtracting a baseline recorded on empty pans under the same experimental conditions.

With the aim to carry out a quantitative estimation of the amounts of calcite and gypsum, the following limits for both DSC peak integration and TG mass loss were used: *i*) calcite decarbonation from 586 to 717°C; *ii*) gypsum dehydration: from 107 to 144°C. The above limits were arbitrarily determined in the flat temperature regions just before and after the peaks in the DTG signals recorded on the standard materials.

X-ray powder diffraction patterns (XRD) were collected at room temperature on finely ground specimens of all the available samples. Records were taken at $K_{Cu,\alpha}$=1.5406 Å, 40 kV voltage, 40 mA current, on a Bruker-D8-Advanced diffractometer fitted with a copper anticathode and a SiO_2 crystal primary monochromator. With the adopted experimental set up, the presence of minor components is not significantly detected below 1%.

IR spectroscopy measurements were collected at room temperature with a FT-IR Jasco 410 apparatus. The powder samples were mixed with KBr as dispersive agent.

Results and discussion

Thermal behaviour

Thermal measurements were carried out on all the available samples. In the following, the thermal response recorded on two samples, namely 1A and 1U, will be presented in detail.

In Figs 2 and 3, the thermal records of the above mentioned samples are illustrated.

In Fig. 2, the DSC trace shows a tiny endothermic effect related to the dehydration of gypsum below 200°C, followed by a larger endotherm between 550–700°C due to the calcite decomposition. In the TG curve the mass losses appearing below 200°C and around 600°C correspond to the phenomena brought out by DSC and are clearly apparent in the DTG curve.

Similarly, Fig. 3 shows both the DSC, TG and derivative TG curves of sample 1U where the calcite decomposition is apparent but the gypsum dehydration is missing.

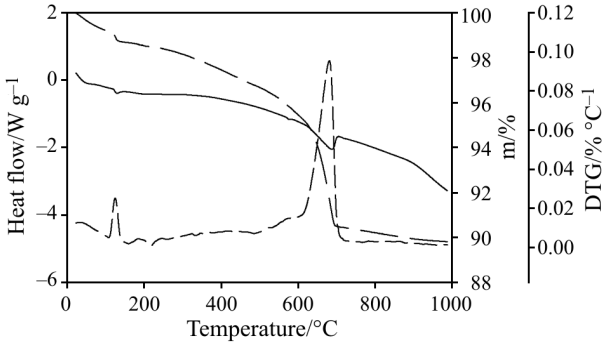

Fig. 2 DSC (——), TG (– – –) and DTG (- - - - -) records of sample 1A plaster

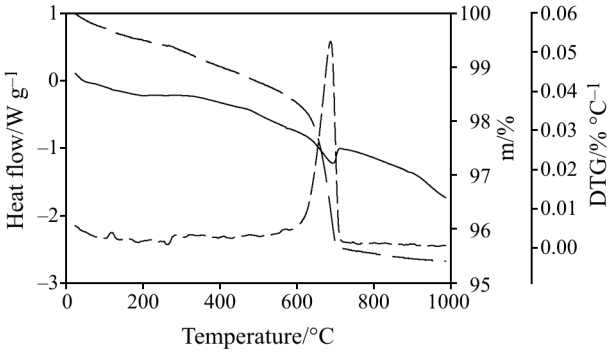

Fig. 3 DSC (——), TG (– – –) and DTG (- - - - -) records of sample 1U plaster

In both samples, a continuous mass decrease between 200 and 500°C was recorded. This phenomenon, along with the calcite decomposition was observed in all the examined samples.

The DTG curves in both Figs 2 and 3 allow a better interpretation of the TG traces: in Fig. 2 the gypsum and calcite peaks are apparent whereas in Fig. 3 only the latter one can be detected. Besides, from 200 to 500–600°C the nearly flat derivative signal indicates that no decomposition of a well definite chemical compound seems to be observed, and hence suggesting the absence of calcium hydrated phases, such as those occurring in common cement and mortar pastes. An example of the latter behaviour was recently provided by Šesták *et al.* [5].

The thermal data determined on the considered samples are reported in Tables 2 and 3 for plasters and mortars, respectively. These results could be subdivided in this way, since they are related to two distinct groups of samples, i.e., those taken near the wall surface (Table 2, where for sample 1 the average from two different samples is tabulated) and those taken inside the wall (Table 3, where for sample 5 the average from two different samples is tabulated).

From Tables 2 and 3 one can remark that the subdivision into two groups of data is consistent with the hypothesis of the existence of two rather homogeneous groups of materials: the plasters set up on the surface of the walls and the mortars employed inside the same walls. This observation leads one to think that the two groups are likely related to two different periods of construction, i.e., the restoration around the end of the 18th century in which new plasters might have been applied on the surfaces, and the building period around the middle of 15th century when the walls were built.

From Table 3, it can be noticed that in the yard of the 15th century mortars were used with a calcite content of the same order of magnitude of those already found in other buildings of the historical palaces of

Table 2 Enthalpy changes and mass losses for the samples of plasters

Sample	ΔH/J g^{-1}	Deviation	Δm/%	$CaCO_3$/%	Deviation
1A+1B	178.6	+15.7	7.15	16.3	–0.15
2A	144.0	–18.9	8.50	19.3	+1.35
3C	116.1	–46.8	5.00	11.4	–2.15
4A	189.7	+26.8	7.80	17.7	+0.65
5B	186.2	+23.3	7.80	17.7	+0.65
average value	162.9	±26.3	7.25	16.5	±0.99

Table 3 Enthalpy changes and mass losses for the samples of mortars

Sample	ΔH/J g^{-1}	Deviation	Δm/%	$CaCO_3$/%	Deviation
1U	71.5	+7.7	2.7	6.1	–0.04
2B	55.0	–8.8	2.5	5.7	–0.24
3B	69.2	+5.4	2.2	5.0	–0.54
4B	88.8	+25.0	4.2	9.5	+1.46
5C+5D	34.6	–29.2	2.5	5.7	–0.24
average value	63.8	±15.2	2.7	6.1	±0.5

Pavia [6, 7]. From the comparison of the two tables one can conclude that the building yard of the 18th century made use for fabricating the plasters of mixtures much richer in calcite than those of the mortars in the original walls.

As a final remark, the gypsum present in the 1A sample was also detected in the 2B one, not shown. Its concentration reaches an amount of ~2 and ~1 mass%, respectively.

XR powder diffraction

The patterns of the two above mentioned 1A and 1U samples are shown as an example in Fig. 4, together with those of two relevant standards, i.e. calcite and gypsum, and one of sand, for comparison.

From the exam of the figure, in both the patterns of the illustrated samples, all the reflections of sand are present, but for a peak at $2\theta \approx 51°$ in sample 1A. The diffraction peaks of the sand were found in all the materials investigated, thus proving that a sand qualitatively very close to that taken as a reference was used for preparing the mixtures employed in these building yards.

Of course the pattern of calcite is well apparent in all the studied materials and, in particular, in the patterns of the 1A and 1U samples illustrated in the figure. On the other side, the presence of gypsum was brought out only in the pattern of the 1A sample, as well as in the one of the 2B material (not shown here). In any case, after a thorough exam of all the collected X-ray diffraction patterns, the presence of common cement components could be ruled out, at least within the detection limits of this technique.

It was beyond the aim of the present paper to carry out a semi-quantitative evaluation based on the diffraction peaks since a reliable calibration system of this technique was not available, and the uncertainty of the data is intrinsically high. Nevertheless, the fair qualitative agreement between the diffraction and thermal data obtained is worthy of mention.

IR Spectroscopy

Fourier transform infrared spectra recorded at room temperature on the studied samples and on the standard materials display a behaviour similar to that of X-ray patterns. In Fig. 5 the IR spectra of the selected 1A and 1U samples are presented, with those of calcite, gypsum and sand.

In the traces of both 1A and 1U samples all the transmittance bands pertinent to calcite are easily detected. For instance, between 1400 and 1600 cm^{-1} is clearly apparent the C=O bond stretching.

In the spectral region ranging between 3000–3700 cm^{-1}, the O–H bond stretching due to the different forms of water can be seen in both the illustrated samples. In particular in the 1A sample the double peak between 3200–3600 cm^{-1} is analogous to those singled out in the gypsum standard and hence related to the crystallisation water of calcium sulphate.

The experimental evidence collected with the various techniques mentioned allows one to confirm the hypothesis that the layers of mortars inside the walls, with a calcite content of about 6 mass%, belong to the origi-

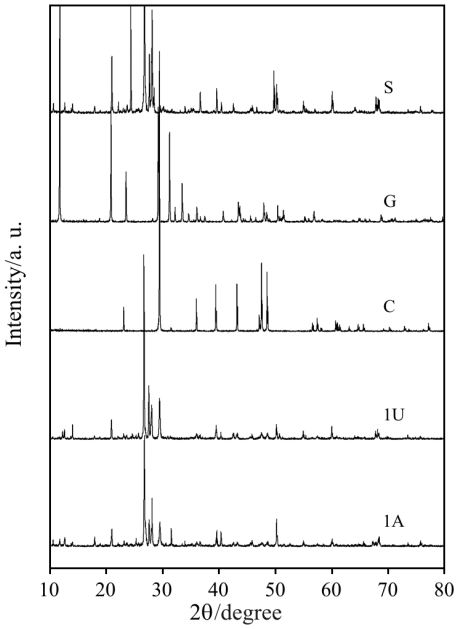

Fig. 4 X-Ray diffraction patterns for the 1A and 1U samples and for standard materials: C – Calcite, G – Gypsum and S – Sand

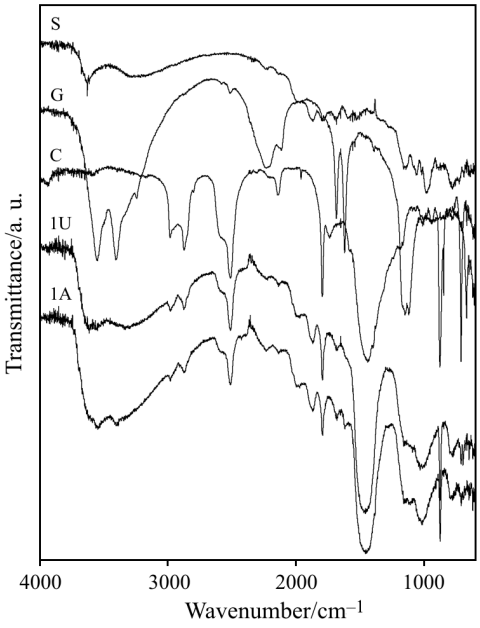

Fig. 5 IR spectra taken on the 1A and 1U samples and on standard materials: C – Calcite, G – Gypsum and S –Sand

nal building of the 15th century; whereas the plasters containing about 16.5 mass% of calcite may be assigned to the restoration works of the 18th century.

This noticeable difference can hardly be attributed to a different degree of carbonation of the original limes used in the mortar and plaster compositions by the carbon dioxide of the air. In fact: *i*) it should be remembered that the carbon dioxide content in the atmosphere of Pavia did not change significantly from the 15th to the 19th century; *ii*) no other hydrated calcium phases were detected on both series of samples by means of XRD. This behaviour turns out to be quite different from that found by Stepkowska *et al*. [8].

The data coming from the thermal techniques, however, suggest that the mass losses observed between 200 and 550°C, being not associated to any evident DSC features, are likely to be related to the presence of other components in the materials. On the other hand, as mentioned above, other calcium salt phases usually present in hydrated cement and mortar pastes could not be detected in the examined samples by means of X-ray powder diffraction analysis.

A deeper insight of these phenomena required a thorough investigation of the thermal behaviour on the standard materials, in particular the inert component, i.e., the sand. In fact, it was found that the TG records on sand samples brought out a mass loss within the above mentioned temperature range, possibly due to the gradual elimination of –OH groups. Therefore, it seemed useful to try to reproduce the 1A and 1U samples by combining the pure components in the proportions detected so far. Figure 6a and b reports as an example the TG traces for the ancient materials of the 1A and 1U (solid lines) samples together with those of the materials reproduced in the laboratory.

As for the 1U material (Fig. 6b), the reproduced specimen (dash-dot line) looks very close to the original sample but for the low temperature range, in which it displays a slightly higher humidity content. In the case of the 1A sample (Fig. 6a), the TG trace of the freshly prepared material (dash-dot line) displays a fair reproduction of both the gypsum dehydration and the calcite decomposition, but as for the total mass decrease it gives a result about 0.5% lower. Such a difference is apparent in the range 250–600°C and is likely to be related to the dehydration of other components, possibly present in the ancient materials.

In order to account for these discrepancies, one might consider the hypothesis that pozzolanic materials were also used in both the 15th and 18th centuries building yards. As reported by Bogue, 'between the 12th to 14th centuries, the quality was improved and this again was noted to be accompanied by thorough burning of the lime and the use of some materials similar to volcanic tuffs previously employed' [9]. How-

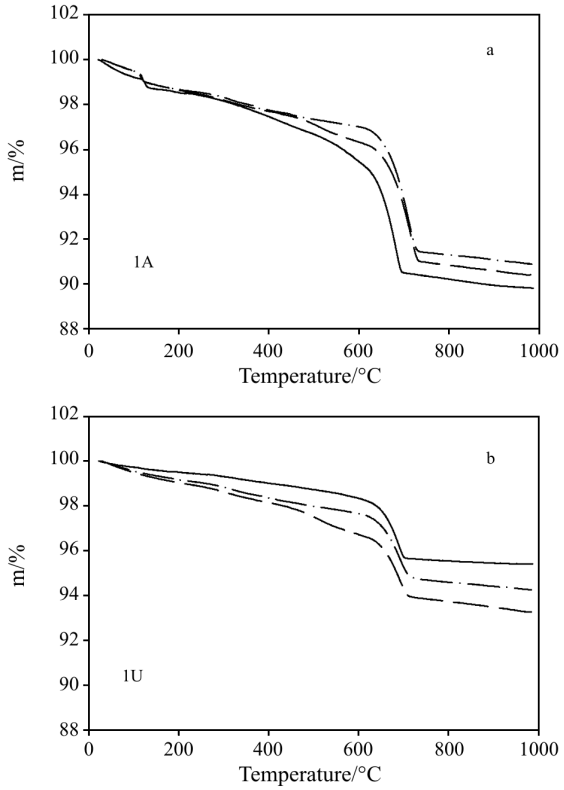

Fig. 6 Comparison of TG curves of ancient and reproduced materials. a – 1A plaster: ancient material (———); new material (– · – · – · –); new material +5% kaolin (– – –). b – 1U mortar: ancient material (———); new material (– · – · – · –); new material + 5% kaolin (– – –)

ever, in the present work no evidence of pozzolanic materials and their reaction products were found by means of the mentioned experimental techniques. Besides, by optical analysis of thin sections of the samples (to be published [10]), the presence of both natural and artificial pozzolanic materials was ruled out. Moreover it is well known that in Pavia and in its district pozzolanic materials neither are found in nature nor were employed in historical buildings [11].

An alternative hypothesis to interpret the DSC and TG results might be to admit the presence of clays in the original building materials. Thus, we thought it suitable to add a fraction of different clays to the reproduced samples, by choosing in particular montmorillonite and kaolin. Since the preliminary thermal data collected on montmorillonite were not encouraging, a little amount of kaolin (5 mass%) was added to both the 1A and 1U reproduced compositions, although this component was not detected by the X-ray diffraction analysis on the original samples. In Fig. 6a and 6b the pertinent traces are represented by the dashed lines. This experiment gives a fairly good result for what concerns the 1A plaster, whereas in the case of the 1U mortar the addition of this clay leads to a divergent result. Such an evidence allows one to

think that the sand used in the mixture prepared in the 15th century was purer than that employed in the 18th century building yard. Further work has been undertaken to clarify this point [10].

Conclusions

Plasters and mortars taken from the walls of the ancient San Matteo hospital in Pavia (Italy), now a part of the central building of the University, were investigated.

The combination of thermal analysis and XRD allows one to state that all the examined samples do not contain components of common cement. Neither natural nor artificial pozzolanic materials, as those of 'cocciopesto', were detected.

By means of the calorimetric and thermogravimetric techniques of analysis, two groups of building materials have been brought out: the first group, corresponding to the plasters of the surface, is remarkably richer in calcite than the second group, formed by the mortars sampled inside the walls.

The high concentration of calcite in the plasters of the first group may be related to the restoration works carried out at the end of the XVIII century.

It was proved that the calcite content in the samples of the second group, probably belonging to the XV century, is similar to that which was determined in other roman and middle-ages mortars sampled in buildings of Pavia.

An experimental reproduction of the ancient materials suggest that the mixtures composing the plasters of the 18th century restoration were made with a less pure sand than those forming the mortars employed in the 15th century building yard.

For a deeper characterization of the building materials, in connection with the various subsequent works and periods of restoration, further work is in progress, in particular by means of thin section analysis.

Acknowledgements

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