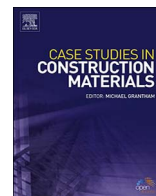




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## Case study

# A study on the cement-based decorative materials in the San Fedele Church in Milan



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## ABSTRACT

Cement-based materials have been used since the 19th century for different decorative purposes, and a high levels of expertise has often reached in reproducing or restoring even quite elaborated stoneworks. An important example is the application of cement-based decorative materials on the façades of the San Fedele church in Milan. The church, built in the 16th century and characterized by the presence of pinkish-yellowish Angera stone on the façades, was subjected, especially in the 20th century, to several restoration works. Damaged decorative elements of the façades as well as portions of its structural elements were replaced or covered in the last century by “stone imitating render”, made with cementitious materials which imitate the original Angera stone. In this study, several samples of cement-based decorative materials, collected from different elements of the external façades of the Church, were characterized by several analytic techniques (thermogravimetric analysis, X-ray diffraction, scanning electron microscopy and IR analysis), in order to investigate both their microstructure and composition, how the chromatic aspect of the cementitious materials were obtained and their conservation state and to provide useful information for the possible reproduction of materials with comparable appearance to be used in a further restoration project. Results showed that the cement-based materials and decorations were obtained by the application of different layers of renders; in particular, the colour and texture of finishing layer were achieved by blending the binder with fine dolomite particles, probably obtained by grinding the Angera stone. This technique not only allowed an amazing reproduction of the original stone, but also resulted in a durable protection, since the cement-based decorative materials did not show any significant degradation phenomena in the polluted environment of the centre of Milan.

## 1. Introduction

In the restoration of historical buildings the characterization of ancient mortars and renders, used for the masonry structures and decorations, is crucial in order to fulfil conservation requirements aimed at preserving the original materials or integrating them with new compatible materials which simulate the original ones [1–5]. As a matter of fact, in the restoration works made in 19th and 20th century, decorations in “stone imitating render” made with cement-based materials [6–8] are often present in many buildings in Northern Italy, and the San Fedele church in Milan (next to the Scala Theatre) is an outstanding example [9].

San Fedele church was built around the former small church called *Santa Maria alla Scala in San Fedele* and it was partly designed by Pellegrino Tibaldi in 1569, as an assignment from Saint Carlo Borromeo. Tibaldi’s work was continued by Martino Bassi, and the dome and crypt were designed by Francesco Maria Richini. Down through the century, but especially in the 20th Century, due also to

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Fig. 1. Main (a) and left (b) façade (b) of San Fedele Church.

the damages occurred during the Second World War, several restoration works were carried out [10].

The church has a main façade, exposed to south-west, of two orders (indicated as *I* and *II*) with a total of twelve pillars made of Angera stone, donated by S. Carlo Borromeo, with a gable on the top. Due to the urban contest of the centre of Milan in which the church is placed, the left façade, exposed to North-West, is conceived in close unity with the main façade (Fig. 1). In the left façade the two orders are separated by a massive belt-course and the columns mark spaces of different dimensions, with niches or rectangular elements (the latter indicated as *sfondati*) (Fig. 2).

The structure of the church is mainly made by brick masonry. The masonry is covered by Angera stone, a dolomia with pink and yellow colouration, extracted around the Maggiore Lake in Northern Italy; some structural (columns) and decorative elements are entirely made of Angera stone. Unfortunately, due to high porosity and calcareous composition, this stone is highly susceptible to atmospheric damage, especially in the urban environment of Milan [11]. The damage on the façades was observed since the early decades of the 20th century and the deteriorated decorations and renders were replaced with cement-based decorative materials, which imitated the original stone.

Restoration works were reported in the historical literature, for instance in the 1950s and in the 1960s, however no detailed documentation is available. In the 1970s the cleaning of the main façade through a sandblasting and the application of ‘polymer paint’ are reported; consolidation with ‘resins’ are mentioned on the elements of the left façade. In the 1980s the paint applied on the main façade was removed and the surfaces were consolidated with the same ‘resin’ used for the left side [10].

At the beginning of the 21st century a new conservation restoration project aimed at the conservation of the external façades of the church was carried out [12]. In order to support these intervention strategies, in 2003, a detailed investigation on the cement-based decorative materials used as stone imitating render and their conservation state was carried out. In this study, the cement-based decorative materials of the San Fedele church were characterized on the basis of X-ray diffraction and thermogravimetric analysis, FT-IR analysis and scanning electron microscopy in order to determine their structure, composition and conservation state. Possible

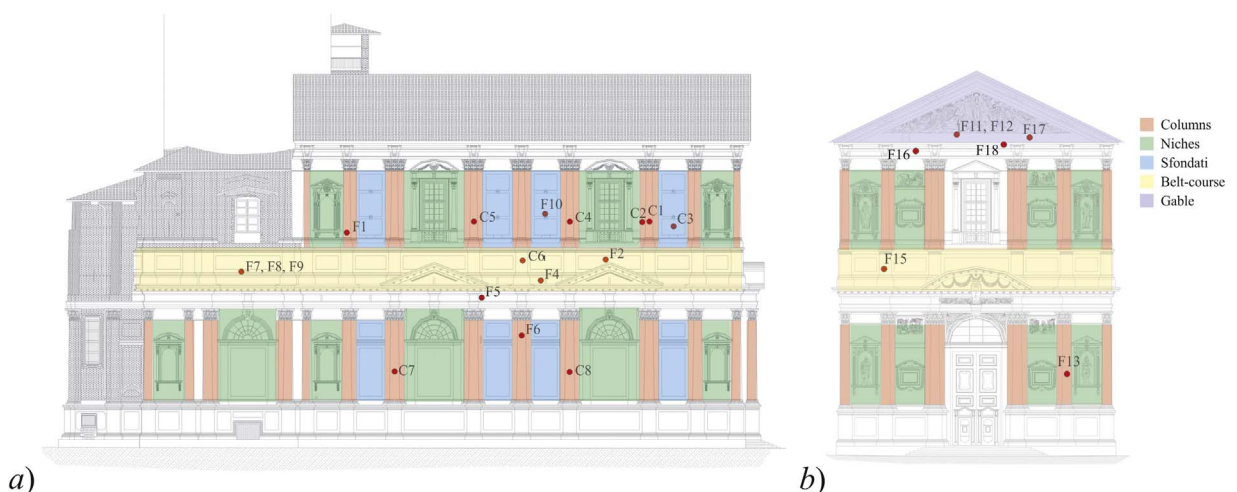


Fig. 2. Indication of the main elements and sampling: left side (a) and main façade (b) of San Fedele Church.

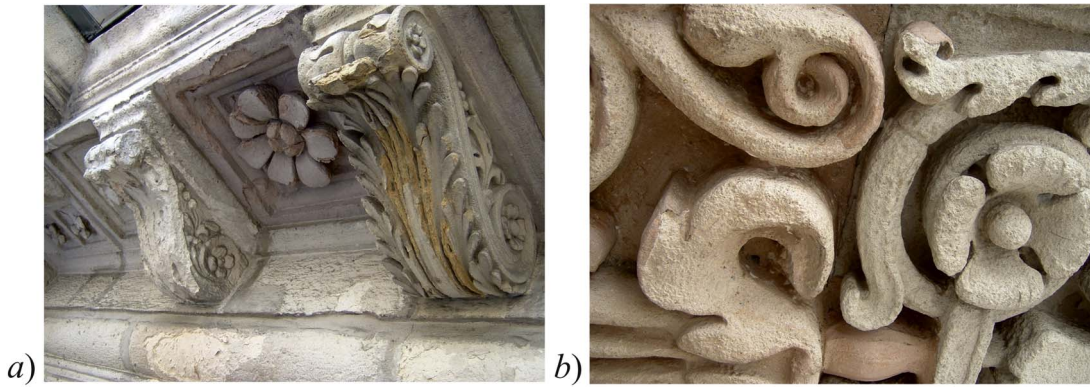


Fig. 3. Damaged decorations in Angera stone on the left side (a) and well preserved decorations made in cementitious materials on the main façade (b).

analogies or differences among the cement-based decorative materials, which have been applied on different construction elements of the external façades and which could be traced to different repair campaigns, were also investigated.

## 2. Inspection and sampling

The façades of the San Fedele Church are characterized by the presence of renders and decorations in cement-based materials, which imitate in texture and colour the Angera stone. Renders are present on the elements of the church as the columns and the *sfondati*. The inspection revealed that the decorations, predominantly present in the main façade, under the gable are similar in the shape, but not in the materials, to those present in the left façade. In fact, those present in the left façade are made in Angera stone and showed, at the time of inspection, a high level of degradation, with exfoliation, granular disintegration and scaling (Fig. 3a), whilst those in the main façade are made with cement-based decorative materials and showed a better state of conservation (Fig. 3b).

To characterize the different types of materials and evaluate their state of conservation a sampling was carried out. Fragments were taken manually, especially in those areas where materials appeared to be damaged, while other samples were cored to define the different layers of materials. Fig. 2 shows the position of the specimens: letter *F* identifies the fragments taken manually and letter *C* identifies the cores. On the left side, 10 fragments and 8 cores were taken (Fig. 2a), whilst on the main façade 7 fragments (Fig. 2b). Finally, for comparison also a sample of Angera stone was collected (*F3*); this sample was already detached from the substrate and hence the exact location is unknown.

## 3. Methods

Fragments and cores were initially observed with the naked eye and with a stereo-microscope, documenting the stratigraphy, the colour of the matrix and of the aggregates.

Subsequently selected samples were gently disrupted, obtaining powders, used for thermal analysis (TG), X-ray diffraction (XRD) and infrared spectroscopy (IR). X-ray diffraction analyses were carried out, in order to identify any crystalline phase of the samples, on the powders using a diffractometer with  $\text{CuK}\alpha$  radiation and a scan rate of  $2.4^\circ \text{min}^{-1}$ . The identification of crystalline compounds was performed by a software (Philips X'Pert SW) and then verified manually with the JCPDS database. Thermogravimetric analyses (TG) involved measuring thermal and mass variation associated with physical and chemical transformations such as dehydration and decomposition; therefore, they were performed to determine also quantitatively some compounds revealed by the XRD analysis and were carried out on the same powders used for XRD analysis. The samples were initially brought to  $70^\circ \text{C}$  and maintained for 20 min with a helium flow of 20 l/min. Subsequently, a temperature scan with rate of  $10^\circ \text{C}/\text{min}$  was started, maintaining the flow of helium, up to  $1200^\circ \text{C}$ . IR analyses were made by means of a spectrophotometer FT-IR in order to identify the unknown components of inorganic and organic nature (also in case of small quantity of sample); on one sample the analysis were performed also after a preliminary extraction with toluene to investigate the presence of organic compounds. Scanning electron microscope (SEM) observations at different magnifications were carried out on gold spattered fragments. The microscope was equipped with an EDS X-ray spectrometer. These analyses were carried out in order to show also at high resolution ( $3000\times$ ) the morphology of main hydration products and particles distributed in the binding matrix, as well as signs of any degradation phenomena. As support for a complete characterization at micro and nano-scale, EDS X-ray spectrometer allowed an elementary semiquantitative analysis.

## 4. Results and discussion

Table 1 lists all the analysed specimens, indicating their location, the stratigraphy, the thickness of each layer and the main results of visual observations. Cores allowed to verify that, in some cases, the column was made with the Angera stone and a layer of cement-based repair render was applied directly on the damaged stone (Fig. 4a). In other cases, the render was applied above burnt-clay bricks as for the columns of the second order (Fig. 4b) or the *sfondati*. Furthermore the macroscopic analysis showed a multilayer

**Table 1**

Samples and summary of results of visual observation, X-ray diffraction, thermogravimetric analyses and SEM analyses.

Location	Sample	Layer	Thickness (mm)	Colour		XRD <sup>a</sup>	TGA <sup>b</sup>		SEM <sup>c</sup>
				matrix	aggregate		% Gypsum	%CaCO <sub>3</sub> (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	
Left side I order	F3	external	–	yellow	n.d.	D	n.d.	– (99.8)	–
	F5	external	–	grey	white	–	–	–	–
	F6	external	–	pink	grey	C, Q, D, S	n.d.	64.7 (59.6)	C, Ca
	C7 <sup>e</sup>	superficial	< 1	yellow	n.d.	C, D, G	11.9	80.0 (73.6)	C, Fe, Mg, Ca, S
	C8 <sup>e</sup>	external	3–9	yellow	white	C, D	n.d.	94.2 (86.8)	–
Left side II order	C8 <sup>e</sup>	superficial	< 1	yellow	n.d.	–	–	–	–
		external	7–11	yellow	white	–	–	–	–
	F1 <sup>d</sup>	external	–	grey	yellow	C, Q, E	n.d.	67.5	Fe, Ti, Mg, Ca
	F10	external	–	grey	black/white	C, Q, G	17.6	52.8	Ca
	C1 <sup>e</sup>	superficial	< 1	yellow/grey	n.d.	–	–	–	–
		external	5–9	grey	black/white	–	–	–	–
	C2	superficial	< 1	pink	n.d.	–	–	–	–
		external	5–9	pink	yellow	–	–	–	–
	C4	superficial	< 1	pink	n.d.	–	–	–	–
		external	2–7	pink	yellow	–	–	–	–
	C3 <sup>d</sup>	superficial	< 1	pink	n.d.	C, Q, G, A, F	8.6	11.4	Fe, Ti, Ca, Mg, S
		external	5–8	grey	grey/white	C, Q, A, D	n.d.	20.2 (18.6)	–
	C5	superficial	< 1	pink	n.d.	–	17.3	57.5	C, Fe, Ca, Mg, S
		external	5–9	pink	grey/white	C, Q	n.d.	76.8	–
		middle	1–3	grey	grey	C, Q, D, A	n.d.	74.9 (68.9)	–
Left side belt-course	F2	external	–	grey	white	–	–	–	–
	F4	external	–	pink	white	C, Q, D	n.d.	66.4 (61.1)	–
	F7	superficial	< 1	pink	n.d.	–	12.2	22.8 (21)	Fe, Ca, Mg, S
		external	3–5	grey	pink	C, Q, G, I	–	–	–
		middle	–	grey	pink	C, Q, D, G, I	5.4	23.2 (21.4)	–
	F8	external	–	yellow	white	–	–	–	–
	F9	external	–	grey	yellow	–	–	–	–
Façade I order	C6	superficial	< 1	yellow	n.d.	–	–	–	–
		external	5–8	grey	yellow	–	–	–	–
Façade II order	F13	external	–	grey	yellow	C, Q, A <sub>r</sub>	n.d.	67.9	C, Ca
Façade I order	F16	external	–	grey	black	–	–	–	–
Façade II order	F18	external	–	grey	white	C, Q, G, E	7.8	77.3	–
Façade belt-course	F15	external	–	yellow	black	–	–	–	–
Façade gable	F11	external	–	pink	white	–	–	–	–
	F12	external	–	yellow	white	–	–	–	–
	F17	external	–	yellow	orange	–	–	–	–

<sup>a</sup> C = calcite (CaCO<sub>3</sub>), Q = quartz (SiO<sub>2</sub>), G = gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), D = dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), A = albite (NaAlSi<sub>3</sub>O<sub>8</sub>), A<sub>r</sub> = aragonite (CaCO<sub>3</sub>), S = siderite (FeCO<sub>3</sub>), E = ematite (Fe<sub>2</sub>O<sub>3</sub>), I = ilmenite (Fe<sub>2</sub>TiO<sub>3</sub>), F = fogsagite (Ca<sub>4</sub>(Si<sub>3</sub>O<sub>9</sub>)(OH)<sub>2</sub>).

<sup>b</sup> n.d. = not detected; – = sample not analysed.

<sup>c</sup> C = carbon, Fe = Iron, Ti = titanium, Ca = calcium, Mg = magnesium, S = sulphur.

<sup>d</sup> Samples taken from *sfondato*.

<sup>e</sup> Samples taken from stone *columns*.

structure of the render. In all the samples a layer (called *external layer*), with a thickness variable in the range 2–9 mm, was present. On some samples a more superficial layer (indicated as *superficial layer*), with a thickness less than one millimeter, was present; it was different in comparison to the more internal ones, especially in the coloration. This might be due to a specific superficial treatment. Only in two samples (C5 and F7) a further layer (denominated *middle layer*) was present between the external layer and the mortar applied on the substrate of bricks or stone.

The *superficial layer* had colours similar to those of Angera stone: in some specimens the colour turned to pinkish in other to yellowish (Table 1). The *external layers* of the cores taken from the columns of the first order (C7 and C8) of the left side had a different aspect in comparison to most of those taken from the columns of the second order (C2, C4 and C5). The matrix of the former appeared to be yellow, with white aggregates with size of the order of millimeters, whilst the matrix of the latter was pink, with yellow and white aggregates with comparable dimensions. This suggests that the skilled labourers that applied the cementitious repair were able to modify the mix composition in order to reproduce the natural changes in colour that characterize the Angera stone. The core C1, taken from the 3rd column of the second order, was an exception: it was characterized by a grey matrix as that of the cores taken from the belt-course (e.g. C6) and from the *sfondati* (e.g. C3). On the basis of observations made during the sampling and through the visual analysis of the samples, it is reasonable to deduce that the *external layer* revealed different intervention strategies: in some case just to cover the bricks, as for the *sfondati*, in other cases to simulate the Angera stone, as for the columns. Where present, the middle layer had a grey colouration. The matrix of the samples of the 1st and 2nd orders of the main façade (F13, F16 and F18) had a grey colouration, whilst the elements of the gable were pink and yellow (F11, F12, F17 and F15).

The visual observations showed high cohesion between the various layers of render and substrate and did not show any type of

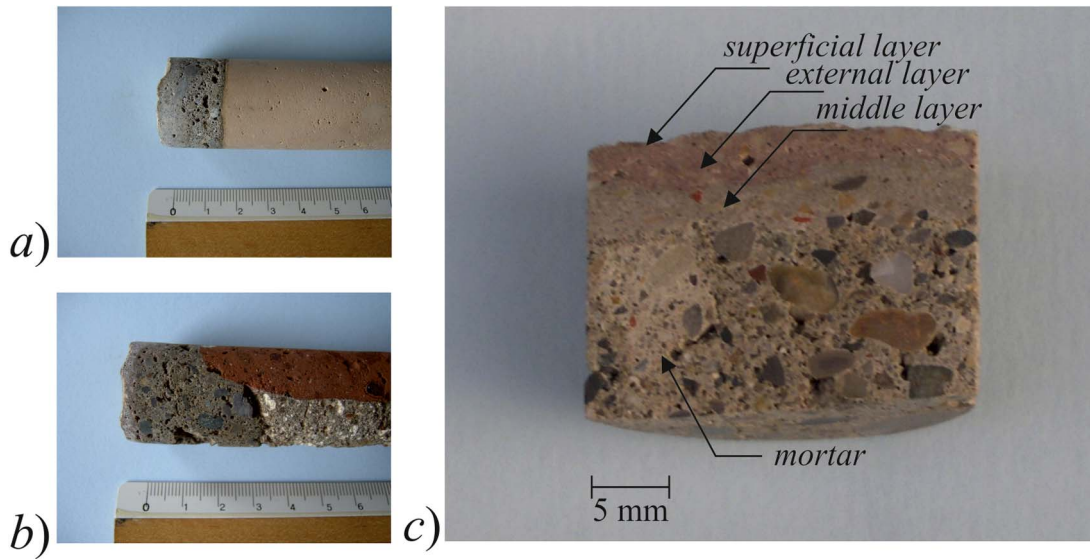


Fig. 4. Example of sample (C1) cored from a stone column (a) and (C4) from a brick column (b) and example of stratigraphy of the sample (C5) from a brick column (c).

damage, suggesting a good state of conservation of the cement-based decorative materials.

Results of XRD, TGA analyses and main findings of SEM analyses are summarized in Table 1.

Although the study was focused on the cementitious materials, also a sample of Angera Stone (F3), which visually appeared yellow and porous, was analyzed. From X-ray diffraction (XRD) analyses the presence of the calcium magnesium carbonate (CaMg(CO<sub>3</sub>)<sub>2</sub>), in the crystalline form of dolomite was assessed (Fig. 5). Fig. 6 shows the thermogravimetric analysis of this sample: a unique relevant mass loss can be observed in the TG curve, at temperature between 550 and 750 °C, which is associated to the decomposition of calcium magnesium carbonate. The mass loss of 47.7% showed that the stone was entirely constituted by dolomite.

Analyses were then carried out on samples of cement-based decorative materials. As far as the composition of the external layer is concerned, in all the samples, the presence of calcium carbonate (CaCO<sub>3</sub>) with the crystalline structure of the calcite (C) and of quartz (Q) was detected through XRD analyses and their peaks were always those of greater amplitude (Table 1). Sample C7 was an exception, since quartz was not observed (Fig. 5).

For those samples with a pink or yellow colouration, the XRD analyses showed also the presence of dolomite (D). In particular, it was observed that the samples of the first order of the left side, especially those taken from the stone columns (C7 and F6), had a higher content of dolomite in comparison to those taken from the second order. Comparing the XRD diffractogram of a sample taken from the first order, as sample C7, with one taken from the second order, as sample C3, it can be observed that in both samples

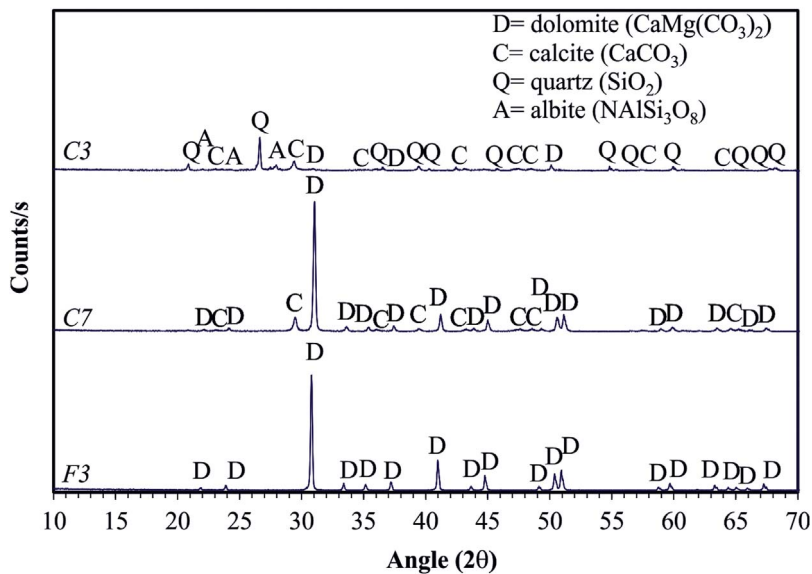


Fig. 5. XRD analyses of samples F3 (Angera stone), C7 and C3.

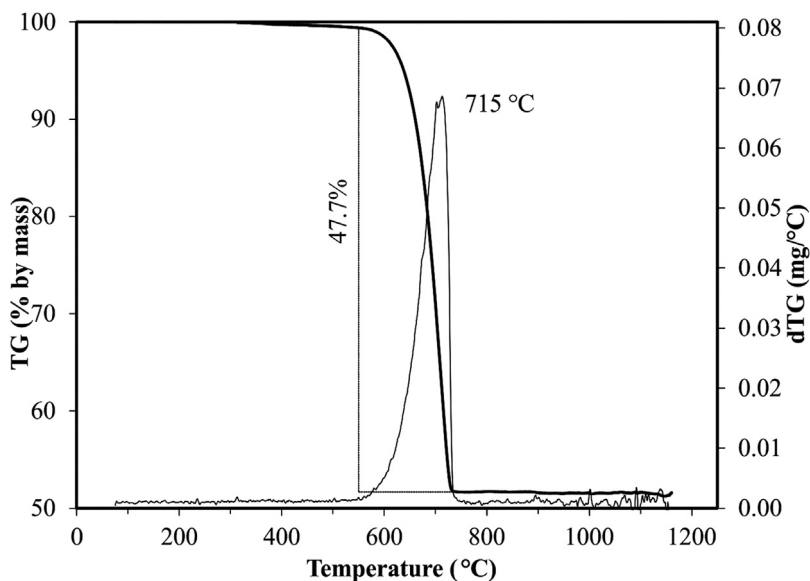


Fig. 6. Thermogravimetric analysis of sample F3: loss of mass of the sample as a function of temperature (TG) and its derivative (dTG).

dolomite was present, however in the sample taken from the second order the dolomite peaks intensity was more pronounced (Fig. 5). In some cases, XRD peaks of other crystalline compounds were detected, which can be attributed to the presence of residual fragments of aggregates in the powders analysed, as, for instance, albite ( $\text{NaAlSi}_3\text{O}_8$ ).

TGA analyses allowed to evaluate the content of calcium carbonate (calcite) detected with the XRD analyses (Table 1). In brackets, the equivalent content of calcium magnesium carbonate is also indicated (Table 1) for those samples that XRD analyses showed the presence of dolomite; as a matter of fact, from TGA analysis the two carbonates cannot be distinguished, since the temperature intervals of dissociation are partially overlapped. In the *external layer*, considering calcium carbonate (calcite) the content varied between 20% and 94% by mass, whilst considering calcium magnesium carbonate (dolomite) the content ranged between 19% and 87% by mass (Table 1).

The observations with the scanning electron microscope and elemental EDS microanalysis showed that the matrix of the *external layer* was prevalently formed by calcium carbonated, as evidenced, for instance, by the presence of calcium, oxygen and carbon in the EDS microanalysis of Fig. 7c, as also detected by XRD and TGA analyses. This did not mean that, originally the binder was a lime mortar; as a matter of fact the calcium carbonate might be attributed to the carbonation of a hydraulic binder. An interesting aspect that emerged from EDS analysis of the areas in which there were particles of calcareous binder, was the presence of silicon (Si) and aluminium (Al). Since the analyses were made on spots and, therefore, directly on the particles that constitute the binder, it should be assumed that these elements had been incorporated in the reaction products. It can therefore be assumed the presence of silico-aluminates and, therefore, of compounds able to confer certain hydraulic properties to the binder [6,7]. These compounds typically are non-crystalline and, therefore, cannot be detected with X-ray diffraction analyses. This observation further supports the hypothesis of the employment of a hydraulic binder that could have contributed to the formation of a denser and more compact microstructure within the hardened paste, hardly compatible with the use of a non-hydraulic binder.

The observations with the scanning electron microscope and elemental EDS microanalysis confirmed the presence of dolomite within the cement matrix in the *external layer* of specific samples. Fig. 7a shows that, for instance, dispersed in the cement matrix, particles of dimension up to 10  $\mu\text{m}$  were present, probably of dolomite, since they were constituted predominantly of calcium, oxygen and magnesium (Fig. 7b). In the samples with higher amount of dolomite, also aggregates of Angera stone, with dimensions of 1 mm, were spread in the matrix. Based on these analyses it is clear that the colour of the *external layer* was obtained by blending the binder with the Angera stone finely ground and, furthermore, using the stone also as aggregate. The analyses showed that in the cement-based materials used for covering the stone columns a considerable quantity of finely ground particles of dolomite was present, whilst those applied on substrate of bricks the dolomite content was less or in some case absent.

The observations with the scanning electron microscope, carried out on the *superficial layer*, revealed that both on the samples taken from the first and the second order, residuals of organic coating were present, in both façades. From the historic documents it emerged that in the second half of the 20th century several consolidating works were made on the façades of the church. The observations showed that the surface was characterized by the presence of darker and compact areas, probably due to the residues of the coating, and by lighter areas of the underlying cement paste (Fig. 8a). EDS microprobe maps of carbon (C), made on a portion of the *surface layer* of sample C5 (column, Left side – II order), showed that the darkest areas were enriched of this element, confirming the organic nature of the coating (Fig. 8b).

Functional groups of this polymer coating were analysed by FT-IR analyses, carried out on a powder sample taken nearby to core C5, Fig. 9. It can be observed that in an un-treated sample the absorption bands of calcium carbonate from the cement-based substrate (with wavenumbers of 804, 1080 and 1464  $\text{cm}^{-1}$ ) interfered with the determination of peaks of organic compounds. Only

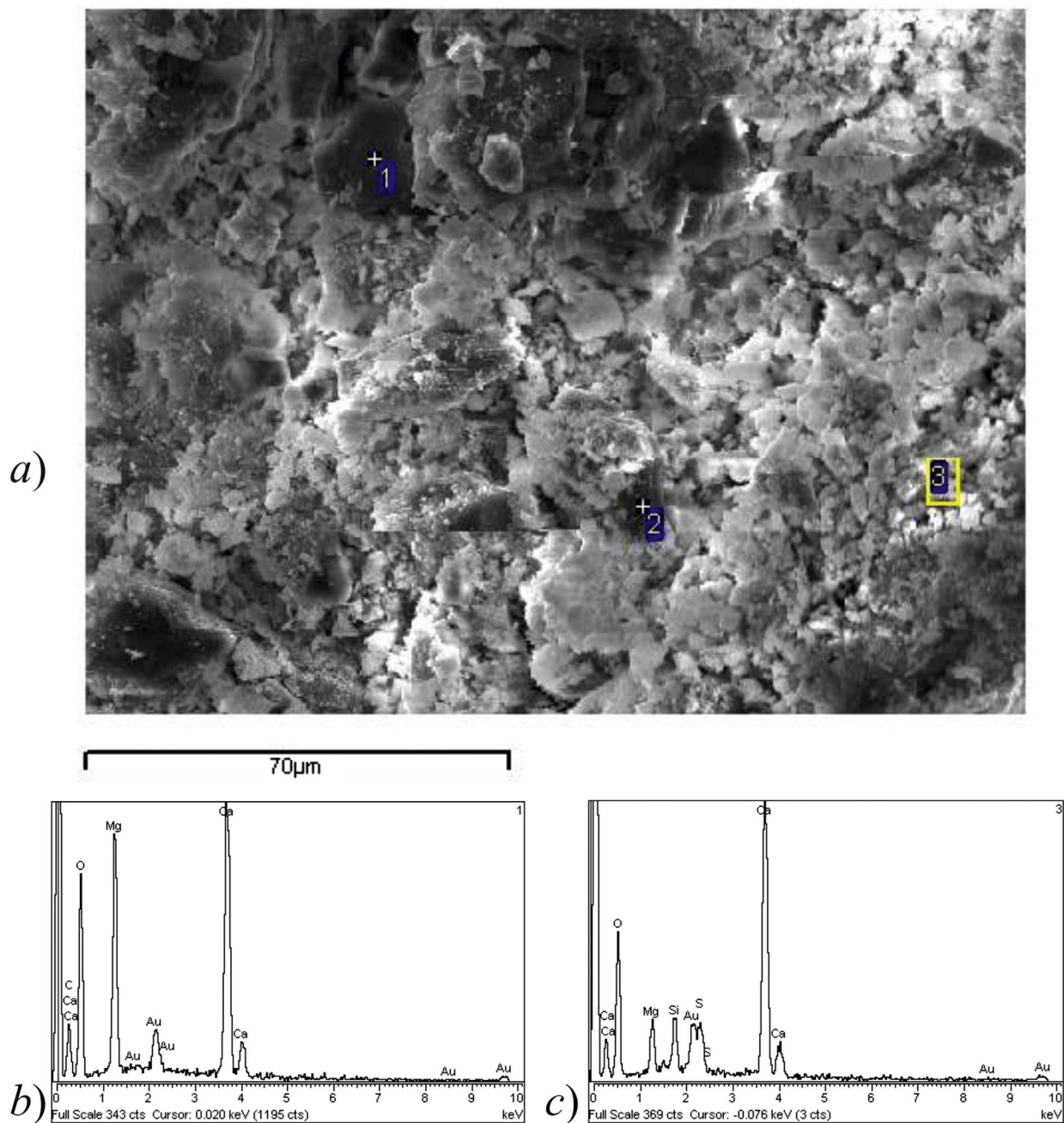


Fig. 7. SEM image of the binder of the external layer of sample C7 (a) and EDS analyses in spots 1 (b) and 3 (c).

after the extraction with toluene (full line in Fig. 9), absorption bands that can be correlated with acrylates (2962, 2918, 2850, 1730 and  $1379\text{ cm}^{-1}$ ), became visible, although a full determination of the organic nature of the coating was not possible [13]. SEM observation clearly showed that only traces of this treatment were present, so that the polymer coating did not affect the performance of the underlying layer.

SEM observation also revealed, on the superficial layer of five samples, the presence of iron and titanium on single particles, which may indicate the use of inorganic coloured pigments (Table 1) to adjust the colouration of the render. As a matter of fact, the main types of synthetic inorganic pigments used to colour historic concrete were iron and titanium oxides, which allow to obtain a red, yellow, brown or black colouration according to the proportions between the binder and pigments and the pigment size [14–17].

On the superficial layer of some samples, among which C7 and C3, XRD analyses showed the presence of gypsum. SEM analysis, carried out both on samples of the main façade, exposed to S-E, and the left façade, exposed to N-W, showed that gypsum particles were present only in the extremely thin superficial layer (few hundreds of μm) as evidenced by the presence of sulphur (S) through

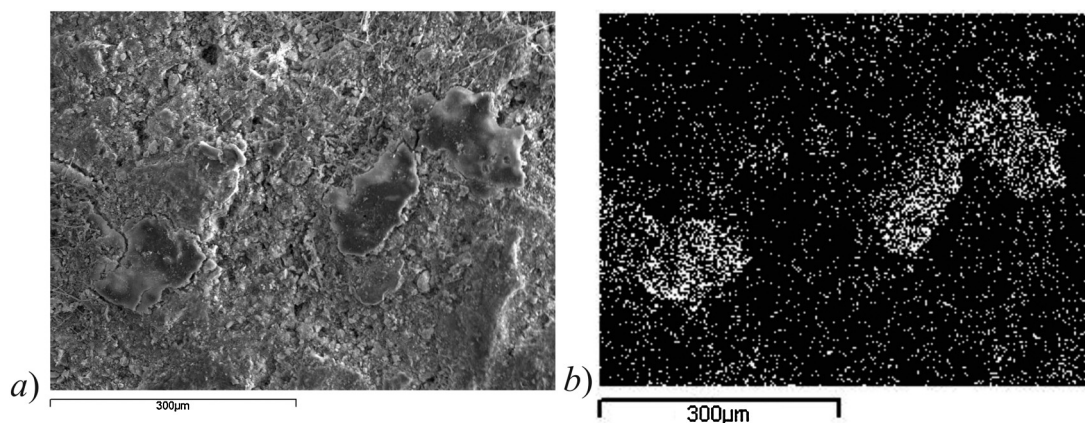


Fig. 8. SEM image of the *superficial layer* of sample C5 (a) and EDS map of carbon (b).

EDS analysis (Table 1). Hence, it might have been intentionally applied with the organic coating (since it was found in correspondence of this) [3]. By means of the thermogravimetric analysis (Fig. 10) the percentage of gypsum present in the samples was evaluated. In the TG analysis the first and last mass losses can be associated with gypsum. The first interval (at temperature lower of 150 °C) corresponds to the loss of water for the formation of hemihydrate and subsequently anhydrite (collectively:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$ ) while the second, at temperature above 750 °C, is associated to the decomposition of anhydrite ( $\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$ ). Hence, through the loss of mass in these two intervals the percentage of gypsum was calculated. For example, in the *superficial layer* of sample C7 (Fig. 10) from the loss of 2.5% by mass observed around 125 °C a content of about 12% of gypsum can be calculated, while from the loss higher of 4.7% at temperatures above 750 °C a content of gypsum higher of 10% can be estimated. Therefore, in this sample, a content of gypsum about 10–12% can be estimated. Where present, the gypsum content ranged between 3% and 17% by mass (Table 1).

Gypsum may also be the result of alteration of calcium compounds due to the effect of sulphur-based pollutants (definitely present, at least since the 20th century, in the urban centre of Milan): in this case the attack was moderate and cannot be considered pathological, since it did not significantly affect the cohesion of the *superficial layer*.

## 5. Conclusions

The study on the cement-based decorative materials showed that the render and decorations applied during the restoration works carried out in the 20th century imitated, with an amazing result, the colour and the texture of the Angera stone, i.e. the construction material which characterizes the façades of the San Fedele Church. These materials were applied in part to repair the damaged elements (both decorative and structural) made with the Angera stone and also to complete the coating of the columns made of

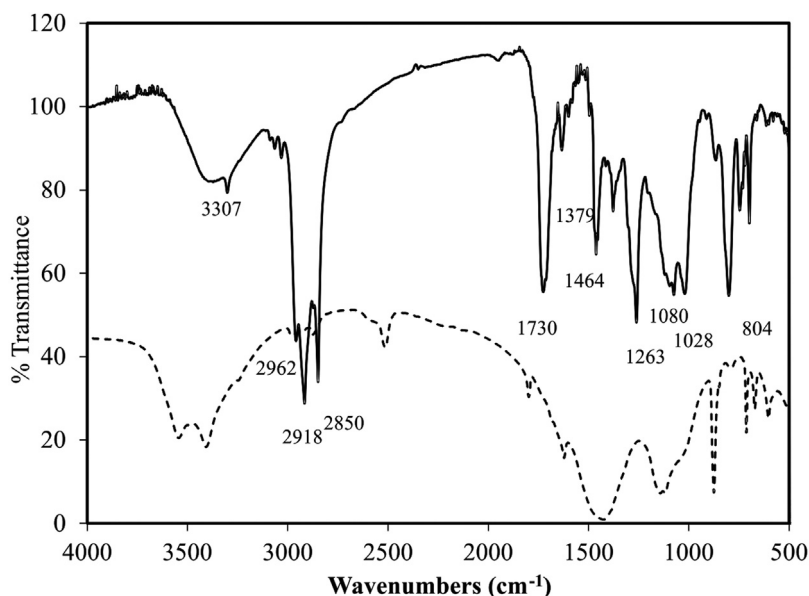


Fig. 9. IR analyses on the *superficial layer* of sample C5 (full line: after toluene extraction; dashed line: without toluene extraction).



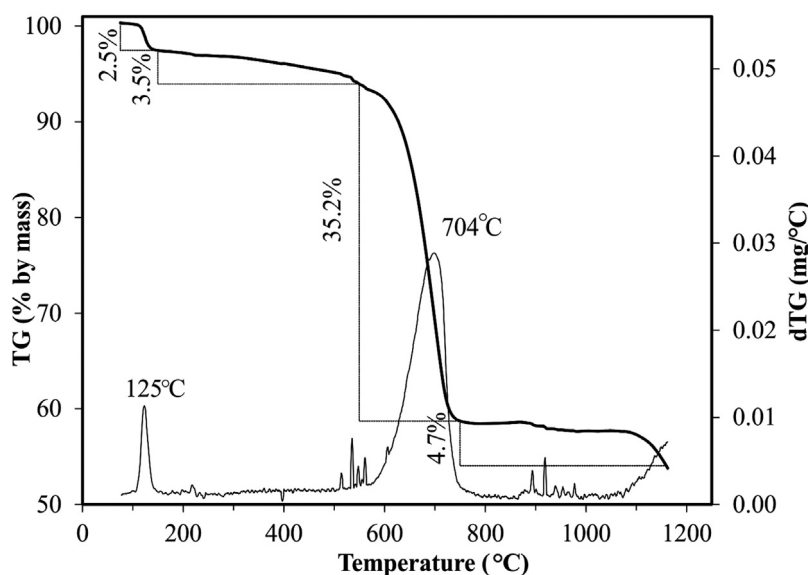


Fig. 10. Thermogravimetric analysis of the superficial layer of sample C7.

bricks. Although the renders used in the reconstruction had an intrinsic variability, the results of the analyses carried out in this work supported the hypothesis of the use of a hydraulic binder. The significant amount of fine dolomite particles presented in the cementitious matrix of the render, suggested that its colouration was obtained, in most cases, by mixing the binder directly with finely ground Angera stone, and also adding Angera stone as aggregate: an increase of its content in the matrix led to a more pinkish-yellowish colour of the render by conferring the typical colour shades of Angera stone.

Inorganic pigments based on titanium and iron oxides were also observed, which might have been added to adjust the colouration of the render.

The cement-based decorative materials showed to provide protection to the underlying materials, both the Angera stone and the bricks. At the time of inspection, no significant degradation phenomena were observed in the cement matrix after exposure to the polluted environment of the centre of Milan. Conversely, surface organic treatments applied in the past have been detected only as residual traces and thus at the current state they would not offer any more protection.

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