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St. Lorenzo Basilica in Milan: Integral approach to characterisation of historical mortars

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Abstract

The work deals with an integral approach to the characterisation of historical mortars coming from the Basilica of St. Lorenzo. The monument, one of the most important of Milan (Italy), has undergone various interventions during the last centuries. At the occasion of a recent conservation work various techniques (optical microscopy on thin sections, X-ray diffraction, FTIR spectroscopy, thermal analyses, ion chromatography) were used in order to thoroughly analyse plasters and bedding mortars from the brick masonry. Investigations from various complementary points of view allowed the identification of the original components of the mortars, i.e. binder and aggregate fraction, and determination of the technology used. Moreover the nature of degradation compounds was elucidated, which enabled us to plan the optimal intervention.

1. Introduction

At the occasion of conservation work carried out for the Jubilee Year (2000), the state of the Basilica of St. Lorenzo[1] in Milan (Italy) has been investigated by characterising the mortars from brick masonry. The first building of the Basilica dates back to the 4th-5th century AD, when it was built using architectural stone elements taken from the nearby Roman amphitheatre. After many building phases and modifications, the building underwent important restoration in the years 1937-1938 by the architect G. Chierici, who brought the church back to its "original shape". Due to the lack of maintenance in the last decades, the plaster coatings by Chierici (referred to as the 'Chierici plaster' in the text) have been deeply decayed and suffered important degradation.

Mortars, being composite materials, are normally investigated by means of various complementary analytical techniques:[2] an integral analytical plan is strongly recommended, as the application of both mineralogical and chemical methods allows us to obtain more reliable and complete results about the binder and the aggregate fractions. X-ray diffraction (XRD) analysis and optical microscopy point out the
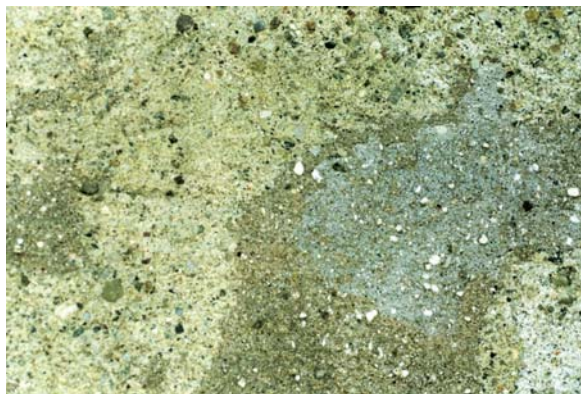
Figure 1: Left: layered plaster decayed by erosion, the upper layer is on the left, the inner layer (grey) on the right. Right: brick masonry with irregular mortar joints.

mineralogical phases[3-6] and are useful in evaluating the stratigraphy of the mortar.[5,6] Porosity is investigated by means of porosimetric analysis.[2] Fourier-transform infrared spectroscopy (FTIR) spectra show the presence of salts and degradation products (nitrates, nitrites, sulphates, carbonates) and point out the nature of the binder (calcite and magnesium carbonate).[3,7-9] TGA analysis provides both qualitative and quantitative information on the binder used in the preparation of the mortar,[10] while with ion chromatography (IC) we can obtain quantitative data on the content of water-soluble salts.[11] After dissolution of the samples in acids,[12-15] studies on their origin are possible by means of determination of metals.[3,16] All these techniques are particularly well suited to verify the state of conservation of the mortars.

In this survey, we report on integral analysis of the mortars from Basilica of St. Lorenzo (Milan, Italy), using various techniques: optical microscopy on thin sections, XRD, FTIR, thermal analysis, and IC.

2. Experimental

2.1 Materials

The upper part of the masonry of the North, East and West sides is covered with the Chierici plasters (Figure 1, left) and an intentionally extensive sampling has been carried out to characterise the materials and to investigate their state of conservation. After a first visual examination of the lower part of the masonry, i.e. uncovered brick masonry, many different restorations and integrations were revealed, and a great number of different bedding mortars (Figure 1, right) were pointed out and sampled. Nevertheless, as the planning of conservation work focused on ancient and traditional materials, the cement-based mortars have been neglected during the sampling. The samples located in the lower parts of walls have been collected in order to establish the salt content due to the water absorption from the ground.

Sample label	Description	Location
L1, L2, L5 ,L7-L9, L11, L13, L15, L16, L23-L26	Plasters Plasters	
L3, L4, L6, L10, L12, L14, L17-L22	Bedding mortars	North side
L27, L28, L30, L32, L34	Plasters	
L29, L31, L33, L35-L42	Bedding mortars	East side
L44, L49-L53	Plasters	
L43, L46, L47	Bedding mortars	Façade
L67- L73	Plasters	
L54- L66,L71,L74-L77	Bedding mortars	South side

Table 1: Descriptions of the mortar samples and their locations.

The samples of plasters and bedding mortars (Table 1) were collected by means of a lancet, according to the UNI-Normal protocols.

2.2. Methods

2.2.1 Microscopy

After the preliminary observations with a Leitz Wild M420XRD stereomicroscope, thin and polished cross-sections have been prepared from the samples according to traditional techniques. Mineralogical-petrographic investigations on thin sections have been performed by a Zeiss standard polarized microscope, while polished cross-sections have been examined using a Leitz Ortholux microscope.

2.2.2 X-ray diffraction

Samples have been ground in an agate mortar as to obtain homogeneous powders. In the event of multi-layered mortars, the various layers have been separately ground and analysed (if possible). The powders have been analysed by a Philips 1130/90 powder diffractometer equipped with a PW 1050/28 goniometer. The diffraction files have been collected in the range 3°-65° (1°/min), using CuKα line (λ = 1.54 Å).

2.2.3 Thermal analysis

The TG curves have been obtained using a Perkin Elmer PC Series TGA-7 thermogravimetric

analyser. The analyses have been performed on powdered samples in the range 30 °C - 900 °C (heating rate 10 °C/min), in a flow of nitrogen gas.

2.2.4 FTIR spectrometry

The FTIR spectra have been recorded using KBr pellets and a Jasco FT-IR 5300 spectrophotometer in the transmission mode, equipped with a DTGS detector, resolution 4 cm^{-1}.

2.2.5 Ion chromatography

Ion chromatographic analyses have been carried out using a Dionex DX 100 ion chromatograph equipped with a Dionex Ion-Pac AS4A column (using Na_2CO_3/$NaHCO_3$ as the eluent) for analysis of anions and with a Dionex Ion-Pac CS12 column (methylsulphonic acid solution as the eluent) for the analysis of cations. The powders have been dried at 60 °C and extracted (100 mg/100 ml) in UHQ water (Ultra High Quality, resistance >18 MΩ). The solutions have been filtered before the injection.

3. Results and Discussion

3.1 Mineralogical investigation

3.1.1 Bedding mortars

Bedding mortars are widely variable in composition according to the many evident renewals carried out in the past, thus preventing any classification or grouping. The binder is composed by traces of calcite and magnesite, sometimes homogeneous, while the aggregate ranged from quartz-silicate and quartz-calcareous sand, with quartz, plagioclase, muscovite and limestone the main components, and with amphibole, chlorite and K-feldspar present in lower amounts, and dolomite detected only in a few samples. The composition of the sand is reminiscent of that from the Ticino River (in the area westward of Milan), characterised by silicate composition, or the one coming from Olona and Lambro rivers which are characterised by calcareous composition (northern part of Milan). In few samples the presence of 'cocciopesto', i.e. broken bricks, has been observed. The poor state of conservation has been confirmed by the presence of high amounts of gypsum, originating in sulphation of the calcitic binder.
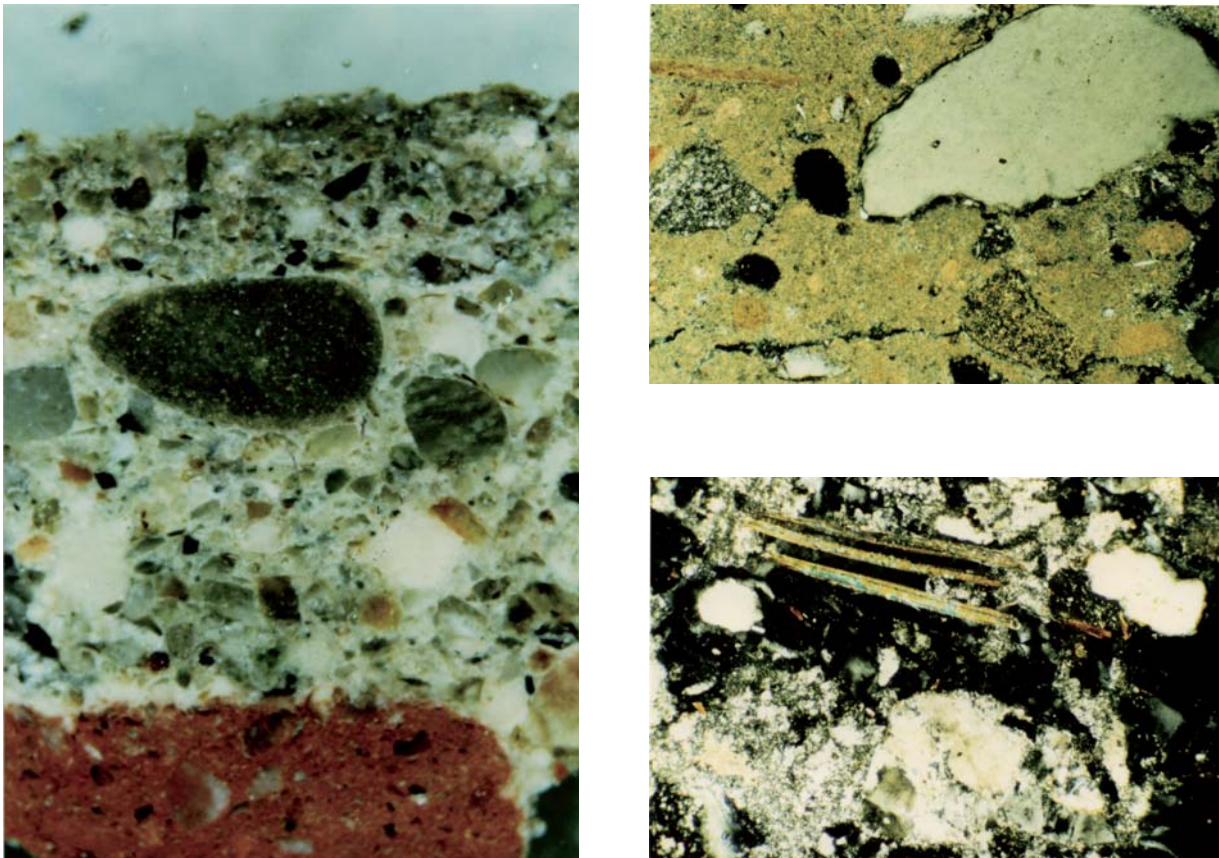

Figure 2: Clockwise from left. Sample L30: brick (on the bottom), mortar layer *i* (thick), mortar layer *m* (grey), mortar layer *e* (on the top); optical microscopy on polished sample. Sample L23: layer *m*: spongy texture with a muscovite tabular crystal (above) and quartz crystals (white); optical microscopy on thin section, crossed polars, 10x. Sample L23: layer *i*: binder texture with cracks and cavities (black), quartz (white) and chert (grey) as sand aggregate; optical microscopy on thin section, crossed polars, 10x.

3.1.2 Plasters

A unique type of a multi-layered plaster has been identified, characterised by the same aggregate as detected in the bedding mortars and by the following stratigraphy (Figure 2, left):

- a first white mortar layer (internal layer, labelled *i*), in contact with the masonry and 5-10 mm thick (Figure 2, right). The binder appears homogeneous and is composed of magnesite and calcite (coming from dolomite outcrops of western Lombardy), while the aggregate is characterised by rounded clasts (0.2-3 mm) of quartz and silicates. In a few samples the presence of cocciopesto has been detected;

- a grey mortar layer (medium layer, labelled *m*), 1.5-3 mm thick; the aggregate is more homogeneous than in the internal layer (Figure 2, right). The binder fraction is the same observed in the internal layer and contains gypsum as the degradation product of calcite;

- a yellow-ochre external layer (external layer, labelled *e*), 250-800 μm thick. Because of the poor state of conservation, this layer cannot be thoroughly characterised. It seems to be composed only by the aggregate and gypsum originating in sulphation processes of the calcitic binder. In most samples the external layer was decayed to the point of being hardly observable or separable (medium-external layer, labelled *m-e*).

The samples from the façade present a unique mortar layer whose thickness ranges between 2.5 and 25 mm; the mineralogical composition is quite similar to that of the internal layer previously described.

3.2 TG analysis

Thermal analyses have been carried out to investigate the nature of the binder fraction and to evaluate the binder/aggregate ratio. The analyses pointed out the presence of calcite ($CaCO_3$) with the characteristic weight loss in the range 589-755 °C due to the calcination reaction, and gypsum ($CaSO_4 \cdot 2H_2O$), with the typical weight loss at 86-157 °C due to dehydration. In Table 2 we present the percentages of calcite and gypsum determined in the various layers of the plasters. In some cases, weight losses have been observed

around 450 °C, due to decomposition of magnesite $MgCO_3$. The percentage of magnesite varies from 3.5 to 11%.

The weight losses characteristic of calcite and gypsum occurred at different temperatures, depending on the conditions of crystallisation: in fact, the decomposition temperature was higher in samples from the internal layer where slow crystallisation led to larger crystals.

The binder/aggregate value as weight ratio (Table 3) has been calculated from the percentages of calcite and gypsum previously discussed, assuming that the binder has been produced from a calcareous stone rich in dolomite and that the gypsum contained in the plaster originated entirely from sulphation of the calcite. Calcite has been assumed to belong only to the binder fraction, although, as already explained, some of it could be part of the aggregate also. As a consequence, the B/A value is only an estimation, allowing us to compare samples and their preparation technology.

Thus, data are presented on multi-layered mortars from plasters of the internal, medium and medium-external layer. The data on the external layers are not particularly meaningful, as the layer could hardly be separated from the medium layer, since a significant amount of gypsum could have been washed out from the surface. Most samples show a B/A value close to 1:3, which is the classical composition of plasters often described in artistic treatises. The B/A ratios of internal layers range between 1/3 and 1/4, indicative of a mortar rich in aggregate, while the medium and medium-external layers are richer in binder (B/A = 1/2-1/3). The samples coming from the façade have highly variable ratios (1/2-1/5), which is probably due to decay of the binder fraction. These values are only indicative of the original ones, but could certainly be useful for production of conservation mortars.

Sample	% $CaCO_3$	% $CaSO_4 \cdot 2H_2O$
Plasters		
Internal layer *i*	8-26	1-8
Medium layer *m*	8-23	2-11
Medium-external layer *m-e*	10-22	9-16
External layer *e*	8-11	10-30
Façade	12-17	8-22
Bedding mortars	7-57	4-17

Table 2: Results of TG analyses of mortars (variability characteristic of single layers).

Sample	Binder (%)	B/A
Plasters		
Internal layer	13-22	1/4
	22-28	1/3
Medium layer	23 -27	1/3
Medium-external layer	27-28	1/3
	30-35	1/2
Façade	16-34	1/5-1/2
Bedding mortars		
L21-L39-L41-L42	58-62	1.5/1
L62	72	1/0.5
L46-L47-L54-L57-L58-L60-L61-L63	42-57	1/1
L6-L40-L71	32-35	1/2
L10-L20-L22-L31-L33-L43-L55-L56-L59-L74	22-28	1/3
L29-L35	20-22	1/4
L12	17	1/5

Table 3: Percentages of binder fraction and binder/aggregate ratios of the mortars estimated from TGA analyses (variability characteristic of single layers).

Sample	F⁻	Cl⁻	NO₂⁻	NO₃⁻	PO₄³⁻	SO₄²⁻	C₂O₄²⁻	K⁺	NH₄⁺	Na⁺	Mg²⁺	Ca²⁺
L24	0.006	0.068	<LOQ	0.267	<LOQ	4.284	<LOQ	0.046	0.014	0.079	0.041	2.238
L25	0.015	0.011	<LOQ	0.065	<LOQ	4.800	<LOQ	0.027	0.014	0.056	0.013	2.028
L26	<LOQ	<LOQ	<LOQ	0.075	<LOQ	2.182	<LOQ	0.026	0.013	0.059	0.285	1.268
L36	0.033	0.377	<LOQ	1.849	<LOQ	10.599	<LOQ	0.177	0.024	0.270	0.351	4.407
L37	0.016	0.022	<LOQ	0.237	0.077	2.656	0.081	0.022	0.012	0.081	0.199	1.446
L38	0.073	0.037	<LOQ	0.972	0.328	5.543	0.081	<LOQ	0.030	0.082	0.043	2.511
L64	0.067	0.026	<LOQ	0.094	<LOQ	8.456	0.141	0.025	0.011	0.063	0.022	4.127
L65	0.113	0.008	0.015	0.046	<LOQ	0.734	<LOQ	0.033	0.016	0.057	0.165	0.318
L66	0.078	0.018	0.005	0.044	<LOQ	0.742	<LOQ	0.041	0.025	0.078	0.270	0.327
L75	0.131	0.048	0.009	0.285	<LOQ	2.310	<LOQ	0.020	0.021	0.080	0.180	1.157
L76	0.099	0.010	0.011	0.036	<LOQ	1.418	<LOQ	0.035	0.028	0.069	0.095	0.695
L77	0.076	0.028	0.008	0.117	<LOQ	2.521	<LOQ	0.029	0.018	0.060	0.152	1.248

Table 4: Results of ion chromatographic analyses (% w/w) of bedding mortars located near the ground (values rounded off to the first uncertain number; LOQ = Limit of Quantification).

Regarding the bedding mortars, the ratios B/A are quite variable and are in some cases characterised by a higher amount of binder than aggregate; such composition is unusual for materials that were supposed to have high mechanical properties and could be ascribed to an overestimation of the binder amount.

3.3 FTIR analysis

FTIR analyses, although limited to external layers, could provide information on both organic and inorganic components. The spectra show the typical absorption bands of calcite (1425, 875, and 713 cm⁻¹), gypsum (3547, 3406, 1685, 1621, 1145, 1122, and 672 cm⁻¹), quartz and silicates (peaks at 1080 and 790 cm⁻¹), sodium and potassium nitrates (1385 cm⁻¹). Nitrates as well as sulphates are typical degradation products found on monuments located in polluted areas. No traces of organic compounds have been found. Not only FTIR Spectroscopy confirmed the results of XRD analyses, in some cases it provided additional clarification on the mortar composition. As an example, the composition of sample L7 seemed quite anomalous, since XRD analysis pointed out only the presence of gypsum. FTIR spectrum of the sample shows the typical pattern of gypsum, quartz and silicates and a weak band around 1425 cm⁻¹, due to calcite (Figure 3). The sample contains calcite as a binder that has almost completely turned into gypsum due to degradation. The presence of calcite has not been found by XRD analysis, as its content is below the detection limit of the technique.

FTIR analysis has been useful in confirming the presence of magnesium carbonates in a few samples, as indicated by the TG curves. In fact, the FTIR spectra showed the typical pattern of magnesium carbonate, as magnesite ($MgCO_3$) or hydromagnesite ($MgCO_3 \cdot Mg(OH)_2$). These compounds could not be easily determined by XRD probably due to their low crystallinity, while in their FTIR spectra a characteristic peak at 1478-1450 cm⁻¹ is evident, due to asymmetric stretching of the carbonate ion in magnesite, and two different absorption peaks at 1420 and 1480 cm⁻¹ in the case of hydromagnesite, due to the presence of two different kinds of carbonate ions in the crystal.[17]

3.4 IC analysis

Bedding mortars located near the ground have been analysed by IC, in order to determine the water-soluble salt content. As shown in Table 4, IC analysis indicates the presence of high amounts of sulphates, probably as gypsum ($CaSO_4 \cdot 2H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$) or epsomite ($MgSO_4 \cdot 7H_2O$), as suggested by the ionic balance. The presence of magnesium sulphates was also confirmed by further XRD analysis. These compounds may be a source of degradation, causing the outbreak of surface efflorescence and also disaggregation as they crystallise inside mortars. The analyses also indicate the presence of phosphate, ammonium and nitrate, presumably originating in animal secretions, garden environment and atmospheric pollution.
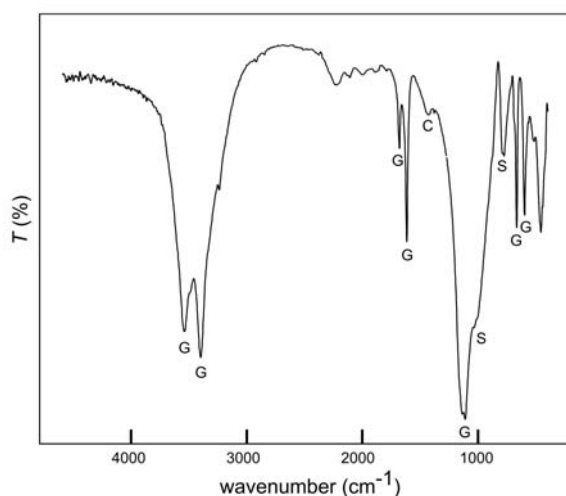

Figure 3: FTIR spectrum in transmission mode of sample L7 [G gypsum: 672, 1122, 1145, 1621, 1685, 3406, 3547 cm⁻¹; S quartz, silicates: 790, 1080 cm⁻¹; C calcite: 1425 cm⁻¹].

4. Conclusions

The mortars sampled from the St. Lorenzo Basilica have been investigated using both mineralogical and chemical techniques. Using mineralogical analysis we determined minerals present both in the aggregate and in the binder fractions and studied the sample structure, while TG analyses provided a reliable estimation of the binder/aggregate ratio. FTIR analyses provided important information on the minor sample components or the components that could not be easily determined with other routine techniques, e.g. magnesite and hydromagnesite. Finally, the contents of water-soluble salts, very important for the evaluation of their state of conservation, have been determined by IC analyses.

The results have led to the following conclusions.

Since the same type of sand has been detected in the internal and the medium layers of the mortars, the two layers may be ascribed to the same period, probably to the well-documented restoration work of Clerici in the 1930s. The poor state of conservation of the external layers has not allowed any hypothesis about their origin, although it is reasonable to assume that they belong to the same application previously described.

The composition of plasters elucidated by the analytical investigations does not provide sufficient information for dating the different interventions, as identical raw materials were determined.

Regarding the bedding mortars, no hypothesis of grouping or dating can been suggested since the composition is very inhomogeneous: on one hand due to the various and many interventions of different nature, on the other hand due to the pronounced degradation, which occurred in brickwork, thus preventing a reliable determination of the composition.

As far as the state of conservation of the whole building is concerned, the presence of high amounts of gypsum and water soluble salts suggests that important degradation phenomena are in progress, typically sulphation of calcite. This may be due to acid precipitations in Milan, while the presence of salts may be ascribed to high amounts of moisture in the walls and in the nearby ground.

Acknowledgements

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