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Characterization of Gypsum-Selenite Plasters from Historic Buildings in the Emilia-Romagna Region (Italy)

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Abstract The use of whole gypsum plasters, i.e. made of gypsum binder and coarse selenite aggregate, still can be found in several historic buildings in Italy (both monumental and rural), but it is absent in historical architectural treatises and totally neglected in current restoration works. The main features of these plasters include good mechanical properties and good resistance, even to outdoor environments, despite their gypsum-based composition; thus, they appear worthy of conservation. In this paper, several specimens of such plasters collected from historical buildings are characterized for the assessment of their formulation, microstructure and state of conservation, as a contribution to the preservation of this interesting technological legacy.

1 Introduction

Materials for architectural restoration must be compatible with the pre-existing ones, not only from an aesthetic point of view, but also in terms of chemical-physical-mechanical properties, since the architectural surface materials actually transmit the building image, as noted by Cesare Brandi [1]. Moreover, the conservation of architectural surface materials (not only structural materials, but also finishing ones, such as plasters) helps to preserve the city’s image and place identity (genius loci) [2]. As a consequence, the characterisation of ancient plasters is fundamental to compatible restoration work, e.g. in order to identify suitable repair materials without disfiguring the building’s image.

In this paper, several plasters, composed of gypsum binder and coarse selenite aggregate (as determined through visual assessment), were taken from different Italian historic buildings in the Emilia-Romagna Region and were investigated. These “whole gypsum” plasters were collected from both indoor and outdoor
walls, as opposed to gypsum stuccoes, which, due to gypsum’s well-known solubility, were traditionally limited to indoor applications. The investigated plasters exhibited a good resistance to outdoor environment and a fair hardness.

It is noteworthy that the formulation of mortars made of gypsum binder and selenite aggregate is totally absent in historical architectural treatises (by Vitruvius, Milizia, Palladio, etc.) and may be connected with the local availability of gypsum quarries. As a matter of fact, local selenite stone was used in Bologna as structural building material since the Middle Ages and as a raw material for the production of gypsum binder. In the 17th century, the gypsum binder from Bologna was known as the hardest in Italy [3].

The plaster samples were characterized to determine their composition and microstructure, as a contribution to the conservation and consistent restoration of such scarcely known material and technology.

2 Experimental

2.1 Samples

The samples of whole gypsum plasters were taken from different historical buildings:

- Santissimo Sacramento [Holy Sacrament] church at Castel Guelfo di Bologna, XVI-XVII century: samples “CG1” and “CG2” are mouldings from the altar in northern side, “CG3” is plaster from a niche in the eastern wall, “CG4” is plaster from a pillar in the western wall, “CG5” is plain plaster from the eastern wall. All samples were originally located in the interior, but the church lost its roof due to bomb damage in the Second World War, so the indoor plasters and mouldings have been exposed to environmental aggression since then.

- San Pietro [St Peter] cathedral in Bologna, XVII century: samples “SP1” and “SP2” are indoor plasters from the bell-tower.

- Malvezzi villa, at Budrio, near Bologna, XVII century: sample “VM” is an outdoor plaster from one of the buildings over the courtyard.

- Homestead and rural building at Torriana (near Rimini), 19th century: samples “T1”, “T2”, “T3” and “T4” are all plain outdoor plasters.

- S. Giacomo [St James] palace at Russi (near Ravenna), 16th century: sample “R1” is plain plaster from the rear portico.

- Selenite is a stone specimen, here named “Se”, from a quarry near Bologna and has been used for comparison.
2.2 Procedure and methods

Freshly chisel-broken plaster samples (about 0.7 g) were dried at 70°C up to constant weight and then analyzed by mercury intrusion porosimetry (Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba, equipped with Milestone 200 software) under the following operating conditions: maximum pressure 2000 bar; cylindrical calculation model; contact angle mercury/material=141.3°. The plaster samples were then characterized by means of X-ray diffraction (XRD, Philips Diffractometer PW1840 operating at 40 kV/20 mA, Cu Kα radiation; the samples were powdered to pass through a 0.075 mm sieve); thermogravimetric analysis (TGA, TA Instruments Thermogravimetric Analyzer Q50, under the following conditions: temperature increase 20 °C/min up to 850°C in nitrogen atmosphere); and by the Dietrich–Frühling method for the determination of carbonate content.

In order to identify the mortars’ components and formulation, with the objective to ultimately reproduce new plasters compatible with the previous one, the samples were manually disaggregated for further tests. Manual disaggregation, required for a reliable separation of binder from aggregate [4], was impossible in dry conditions due to the great hardness of these plasters; therefore, the process was enhanced by a preliminary immersion in distilled water for at least 48 hours (depending on the sample hardness). To confirm the complete dissolution of gypsum binder and the absence of binder residue on the surface of the aggregate grains, the aggregates were observed by a stereo-optical microscope (SOM, Wild M3 Heerbrugg). Then, the aggregates were dried at 50°C for 5 minutes and sieved with standard UNI sieves (6.7–5.6–4–3.35–2–1–0.5–0.25–0.075 mm) under mechanical vibration (10'). After sieving, the single fractions were observed again by SOM and separately investigated through the methods reported above.

3 Results and discussion

The composition and carbonate content of the samples (expressed as CaCO₃, wt%) are reported in Table 1. Most of the samples exhibit a complete or almost complete bi-hydrated calcium sulphate nature, thus confirming that the aggregates are made of selenite. XRD also detected the presence of calcium carbonate (calcite) in some samples; in particular, the samples from Castel Guelfo (CG-series) showed significant amounts of calcite, as well as traces of quartz. The presence of calcite and the good hardness of these samples suggest that the CG plasters were made with a lime-gypsum binder in order to improve their strength and fresh-state workability, as evidenced in [5-6]. The fresh-state workability and hardening time were very important for these plasters, as they were used for ornamental mouldings. No significant abundance of calcite was detected in samples from Torriana and Malvezzi Villa, probably because these plain wall
plasters had no particular workability requirement. SP samples did not contain calcite (and in fact they are not moulded, but plain plasters), while some quartz was present in the SP1 sample aggregate. The traces of feldspars (orthoclase group) detected in CG4 and R1 samples may be attributable to the addition of quartz/feldspar aggregates to the plasters.

Table 1 Results of XRD analysis and carbonate content of the plasters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>G</th>
<th>C</th>
<th>Q</th>
<th>F</th>
<th>CaCO₃, wt%</th>
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<tbody>
<tr>
<td>CG1</td>
<td>+++</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CG2</td>
<td>++</td>
<td>+++</td>
<td>+</td>
<td>-</td>
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</tr>
<tr>
<td>CG3</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>17.6</td>
</tr>
<tr>
<td>CG4</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>15.0</td>
</tr>
<tr>
<td>CG5</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>7.8</td>
</tr>
<tr>
<td>SP1</td>
<td>+++</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
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<tr>
<td>SP2</td>
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<td>T3</td>
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<tr>
<td>R1</td>
<td>+++</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>9.2</td>
</tr>
<tr>
<td>VM</td>
<td>+++</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
</tr>
</tbody>
</table>

+++ = dominantly present, ++ = present, + = traces, = not present,
G = gypsum, di-hydrated calcium sulphate (PDF number 33-311), C = calcite (PDF number 5-586), Q = quartz (PDF number 33-1161), F = feldspar (orthoclase group, PDF number 41-1480).

TGA was performed on powdered samples to determine gypsum content (binder and aggregate) and to highlight differences between the samples and/or the presence of organic admixtures, common in ancient gypsum stuccoes [7]. The TGA-DTG curves of some significant samples are shown in Fig. 1. No organic admixtures were detected in the samples, while gypsum content, calculated on the basis of the weight loss in the range 130-180°C [8], spans from 41% (CG2 sample, lime-gypsum bound) to 96% (T3 sample, whole gypsum plasters). After water immersion and dissolution of the gypsum binder, the aggregates were sieved. The resulting grain size distributions are reported in Fig. 2.

Selenite aggregates were easily detectable by SOM in the sieved fractions (Fig. 3). The selenite aggregate in the Malvezzi Villa plaster was quite coarse, and its low porosity, might improve the plaster’s resistance to environmental decay. The CG3 sample, a quite strong plaster, also exhibited coarse aggregate. On the other hand, the samples from the rural buildings in Torriana, showing a small grain size, appeared quite weak, as the selenite aggregate seemed too fine to provide significant toughness. The use of gypsum in the rural buildings at Torriana seems
linked not to the achieving of particular performances, such as strength or workability, but to its cheapness (due to low firing temperature) and wide availability in the area \([9]\).

After sieving, the aggregate fraction 0.5-3.35 mm was tested for carbonate content, in order to assess whether calcite was present in the aggregate. Results substantially confirmed all findings reported above.

![Fig. 1 TGA results for some significant samples (continuum lines: TG; dotted lines: DTG)](image)

![Fig. 2 Plasters’ grain size distribution curves](image)
The pore size distributions of the samples are reported in Fig. 4. The low porosity of selenite confirms the improvement of strength and durability connected with the use of such aggregate. The wide variability of the curves in Fig. 4 illustrates the different microstructures of the gypsum plasters, surely affecting their hardness.

“CG5” aggregates retained at 1 mm sieve. “T2” aggregates retained at 0.5 mm sieve.

“T4” aggregates retained at 1 mm sieve. “VM” aggregates retained at 1 mm sieve.

**Fig. 3** Stereo-optical microscope pictures of some significant samples

The softer samples (such as T4, T2 and CG4) are highly porous plasters with a large mean of pore radius, while the harder samples, difficult to disaggregate, exhibit lower open porosity (as seen in sample CG2). Hence, porosity and hardness are influenced by both selenite aggregate (abundant and coarse aggregates give harder mortars) and the addition of slaked lime to gypsum binder (apparently the most significant factor). Plasters exhibiting high carbonate content from lime carbonation also are characterised by low porosity.
Conclusions

The characterisation of the gypsum plasters accomplished in this paper confirms that selenite aggregates were used together with gypsum binder. Moreover, this study has demonstrated the role of mixed gypsum-lime binder and coarse aggregate size in improving the mortars strength and durability. The results contributed to an understanding of the microstructure and formulation of gypsum plasters in order to design new compatible plasters for restoration, especially where it is necessary to fully replace older plasters or fill gaps. Moreover, this study is intended to contribute to the rediscovery of an ancient building technique that today is totally neglected.

References

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