Youth in Conservation of Cultural Heritage, YOCOCU 2012

Stucco Forte in Venice between the 16th and 17th centuries: the case study of Addolorata Chapel stuccoes in San Pantalon´s Church

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Abstract

Stucco samples of the 17th century were collected from the Addolorata Chapel in San Pantalon´s church, which represents an important example of the stucco forte technique in Venice. Stucco forte is usually made adding powdered lime and marble to the gypsum base mixture. However, the exact recipe remain in most cases still unknown as often related to the knowledge and experience of the artisans [1]. The aim of the present work is to characterize and study the chemical-physical composition, the working techniques and the conservation state of the stucco forte in Venice. The samples were subjected to optical and electrical microscopic observation (OM, SEM-EDX), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG-DSC), and mercury intrusion porosimetry (MIP). Gypsum, and calcium carbonate were found as major components with presence of magnesium carbonate and traces of hydromagnesite. Magnesite and hydromagnesite do not develop within the normal carbonation processes suggesting that magnesium carbonate was intentionally employed for improving the material characteristics.

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1. Introduction

Stucco has been widely used throughout the centuries as decorative coatings for ceiling and walls for both interior and exterior finishing. It is however during the Baroque period that stucco sees it highest moment for decoration as well as for figurative representation. Stucco provided the ideal material to satisfy the baroque decorative taste, where the real architecture of the building is visually extended into the walls in unreal forms and decorations.

In general, the word stucco identified a material obtained mixing aggregates, a binder and water in different proportions depending on the materials available, the technologies, etc. Many of the receipts are still unknown as often related to the knowledge and experience of the artisans, jealous of their recipes [1-6].

An example of this particular situation is the use of stucco and, in particular, of *stucco forte* technique in Venice between the 16th and 17th century following the growing and development of the Baroque taste. In this period, three different types of stucco can be found in Venice: i) gypsum stucco obtained mixing calcium sulphate hemihydrates, water and additives, such as organic binders and fillers of different nature (sands, talc, marble powder); ii) lime stucco made mixing calcium hydroxide and aggregates or fillers (often marble powder or sand); iii) mixed stucco obtained mixing calcium hydroxide, gypsum and aggregates. Lime stucco and mixed stucco are often referred as *stucco forte*. Different additives were also added to the mixtures for improving the workability, the mechanical properties, or for reducing the shrinkage. Organic binders, inorganic aggregates and fillers are only some of the additives commonly used. The use and the combination of these additives was often considered as artists secret and crucial for the final characteristics of the stucco. The identification and the study of the stucco compositions and techniques are, therefore, important not only from the historical and artistic point of view, but moreover for the selection of the most appropriate approach for their conservation.

In this work the stuccoes of the Addolorata Chapel in San Pantalon's Church in Venice were investigated, revealing a new aspect of the great mosaic of the stucco techniques of the 17th century.

At the end of the 17th century Pietro Roncaioli was commissioned to decorate the Addolorata Chapel after the rebuilding of the church during the 16th century [7-9]. Roncaioli was one of the many ticineese artists active during the Baroque period in Venice and in the Mainland. For the Addolorata Chapel Roncaioli designed a complex decoration of joyous cherubs and angels to embrace the three paints of Giovanni Antonio Fumiani (Fig. 1) located in the church.

The main objective of the present paper is to combine the data obtained via optical and electron microscopy (SEM-EDX), FTIR spectroscopy, thermogravimetric (TG-DSC) and porosimetric analysis (MIP) in the attempt to establish the stucco recipe used by Pietro Roncaioli and in general of the stucco technique in the 17th century in Venice. The characterization of the nature of the raw materials as well as their selection criteria and relative proportions is thus considered the basis for understanding the technological level of the studied artist and moreover for a compatible and correct intervention.

2. Experimental part

A first evaluation of the conservation state of the surfaces was performed thanks to visual observation and weathering maps. Based on these observations and the historical and artistic documentations, small portions of stuccos and degradation products were collected with a scalpel. The samples were afterward transferred in our laboratory and subjected to analysis. Each sample was subjected to microscopic observation and part of them were embedded in resins obtaining polished cross sections. The morphology and the structure of the cross sections were studied by optical microscopy (Olympus SZX16) and electron microscopy with EDX probe (Jeol JSM – 5600 LV, JSM 5600). The evaluation of the granulometric distribution via test sieves and porosimetric analysis, performed with a mercury intrusion porosimetry (Pascal 140 and Pascal240 Thermo Fisher Scientific),

completed the microstructure analysis of the samples. The binder/aggregate ratio (B/A) was also calculated dividing the coarse aggregates from the binder, usually identified with the finer powder (powder diameter < 100μm).

FTIR spectroscopy and thermogravimetric (DSC-TG) analysis were also performed for a complete chemical characterization of the samples. For the FTIR analysis few milligrams of samples were grinded, mixed with KBr, compressed as pellets (10 Tons pressure) and then analyzed using a double beam Thermo Nicolet Nexus 670 FT-IR spectrometer, associated to Omnic E.S.P. 10 software to elaborate the spectra, collected in the range of 4000-400 cm^{-1} with 4 cm^{-1} resolution.

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were performed simultaneously on grinded samples using a Netzsch 409/C apparatus. The analysis were done in Air/N_2 atmosphere at a flow rate of 40ml/min from 30°C to 1000°C, using Pt/Rh crucibles and alumina as reference material. Data was collected with STA Netzsch software and then elaborated with Origin 8 software.

3. Result and discussion

3.1. State of conservation

The conservation state of the stuccoes was in general bad, but non critical (Fig. 1). Disaggregation of the surfaces and presence of salt efflorescences were the major degradation processes. The salt efflorescences created in many case thick and hard crusts that could be hardly separated without damaging the stucco surfaces. The presence of sub-efflorescences were also observed in many areas leading to the detachment and exfoliation of the surfaces. Moreover, detachments of bigger portion of material were observed revealing in many areas the underneath iron rods composing the skeleton of the structure. During this first phase, it was also possible to distinguish many interventions related to previous restorations, recognizable because a brighter and paler stuccoes was applied.

Fig. 1 (a) Vault of the Addolorata Chapel in San Pantalon´s Church; (b) material losses and spalling (c) detachment and rusty iron rods

3.2. Stratigraphy and cross section analysis

Figure 2 shows the cross section of one of the collected samples presented here as an example. Two layers, different for color and structure, can be identified. The inner one, identified as the bulk material, is a dark- grey

stucco with a granulometric distribution (Table 1) of the aggregates in the range of 0,09-2 mm and an average diameter around 0,18 and 0,71 mm. The external or finishing layer is composed of a brighter stucco with aggregates dimension that ranges from 0,09 to 0,18 mm, and average diameter around 0,18mm. In both cases, the binder presents a pale color and is characterized by a microcrystalline texture and homogeneous structure, while the aggregates differ in color and shapes. The aggregates of the bulk are in fact darker, bigger and coarser than the one of the surface-layer with a binder aggregate ratio (B/A) higher for the finishing layer. A higher amount of binder respect to the aggregates allows to obtain a finer and more workable mixture.

   A precise characterization of the microstructure of the bulk was obtained via MIP analysis. The stuccoes are characterized by a high open porosity, around 40%, and a pore radius distribution between 0,1-0,7 μm.

Table 1. Granulometric distribution, residual % mass on different sieves

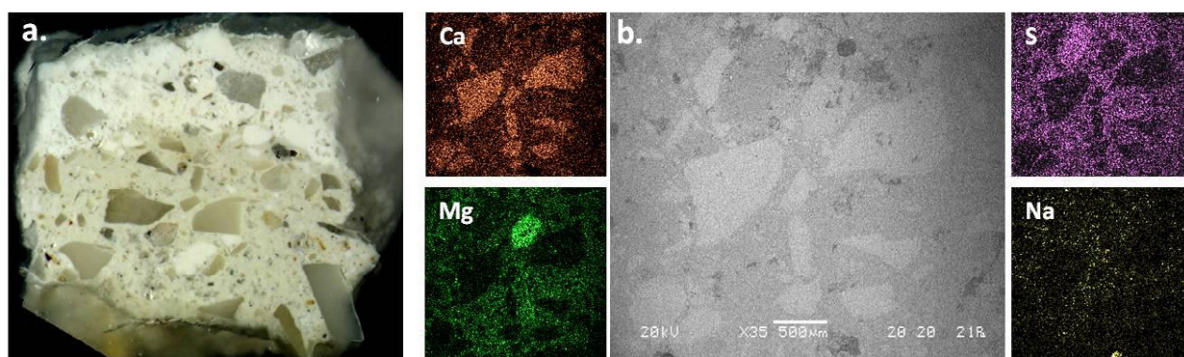| Sieve mesh	Granulometric distribution (mass%)						B/A (by mass)
	< 90μm	90 μm	125 μm	180 μm	710 μm	1000 μm	
Surface layer	33,1	11,3	14,4	40,7	0,5	0	0,80
Bulk	1,4	12,3	16,9	34,7	8,5	26,2	0,16

Fig. 2 (a) Smoothed cross section of sample C15B observed at optical microscope 16X; (b) SEM image of the bulk 35X and EDX elemental maps of calcium, magnesium, sulphur and sodium

3.3. Chemical composition

   SEM-EDX observations provided the qualitative elemental analysis of the samples (Fig. 2). Calcium, sulphur, silicon, and aluminum together with sodium, chlorine and magnesium were detected as mayor elements. Calcium and sulphur show a strong signal in all the samples. However, from the elemental mapping the presence of sulphur was detected only in the binder, while calcium was found in the binder as well as in the aggregates, suggesting that marble powder might have been used as main aggregate. Magnesium was also found in some aggregates and in minor traces in the binder. Silicon and aluminum were also detected in some aggregates of the bulk stuccoes and are probably related to the addition of sand in the stucco mixture. Sodium and chloride were

also detected all over the samples and mainly accumulated in the finishing layer of the statues probably linked to marine aerosol deposition.

Figure 3 (a) shows one of the spectra obtained via FTIR of the samples bulk. The S-O stretching peak at 1143 cm^{-1} and the $-SO_4$ bending peaks at 603 cm^{-1} and 670 cm^{-1} confirm the presence of gypsum as binder both in the finishing layer and in the bulk. Calcium carbonate was also found in all the analyzed samples (stretching peaks of $-C=O$ at 1798 cm^{-1} and 1428 cm^{-1}; bending peaks at 875 cm^{-1} and 712 cm^{-1}). The presence of magnesite ($MgCO_3$) was also suggested by a peak at 746 cm^{-1}, which is the unique peak that differs calcium carbonate from magnesium carbonate [1].

The FTIR analysis of the salt efflorescence products (Fig. 3b) highlights the presence of epsomite ($MgSO_4 \cdot 7H_2O$) identified by the peaks at 1108 cm^{-1}, 624 cm^{-1} and 741 cm^{-1} related to the presence of sulphate groups, and the intense and broad $-OH$ peak at about 3300 cm^{-1}.
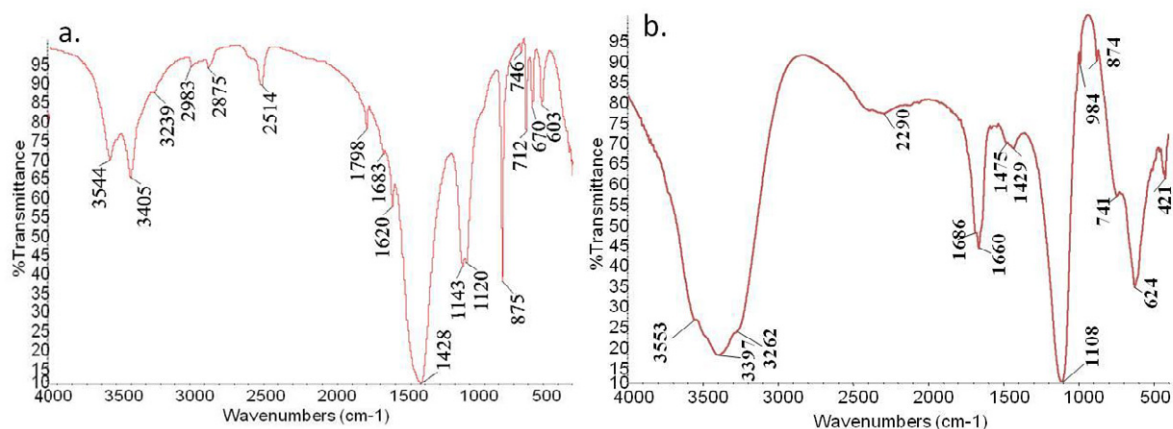

Fig. 3 FTIR analysis (a) bulk sample (b) salt efflorescence

The TG-DSC analysis of the bulk samples confirmed the presence of gypsum and calcium carbonate, recognizable as mass losses between 100-150 °C and 630-780°C, respectively. The lower temperature detected for the transformation of calcium carbonate to calcium oxide, usually at about 700-800°C [10-12] might be related to a partial or incomplete crystallization of the lime added to the stucco as binder. A third mass loss was detected at about 350-480°C in correspondence to an endothermic DSC peak, which can be related to the transformation of magnesium carbonate to magnesium oxide [1]. The thermogram of the finishing layer (Fig. 4 (a)) shows again the mass losses of gypsum (100-150°C), magnesite (350-480°C), and calcium carbonate (630-780°C). Three other small peaks were detected in the DSC analysis: an exothermic peak at about 294°C related to the presence of epsomite and two endothermic peaks at 237°C and 325 °C. The endothermic peaks are indicative of the dehydration of hydromagnesite and of the decomposition of the carbonate and hydrate, respectively [13; 14].

The TG-DSC analysis of sample collected from an efflorescence was also performed (Fig. 4 (b)) for the identification of the degradation compounds. A first strong mass loss was detected between 50-200°C with a correspondent DSC endothermic peak centered at 101°C, which can be related to the dehydration reaction of epsomite and the formation of $MgSO_4 \bullet 0,1H_2O$ [15]. A second mass loss, correspondent to an exothermic DSC peak, was also found at about 290°C and it is probably related to the transformation of amorphous $MgSO_4 \bullet 0,1H_2O$ to crystalline $MgSO_4$ [15]. The reactions involved in the process can be schematized as follows:

$$MgSO_4 \cdot 7H_2O \rightarrow MgSO_4 \cdot 6H_2O + H_2O \quad \text{at} < 50 \text{ °C, not observed} \tag{1}$$
$$MgSO_4 \cdot 6H_2O \rightarrow MgSO_4 \cdot 0,1H_2O + 5,9H_2O \quad \text{at } 101°C \tag{2}$$
$$MgSO_4 \cdot 0,1H_2O(s) \rightarrow MgSO_4(s) + 0,1H_2O(g) \text{ at } 293°C, MgSO_4 \tag{3}$$
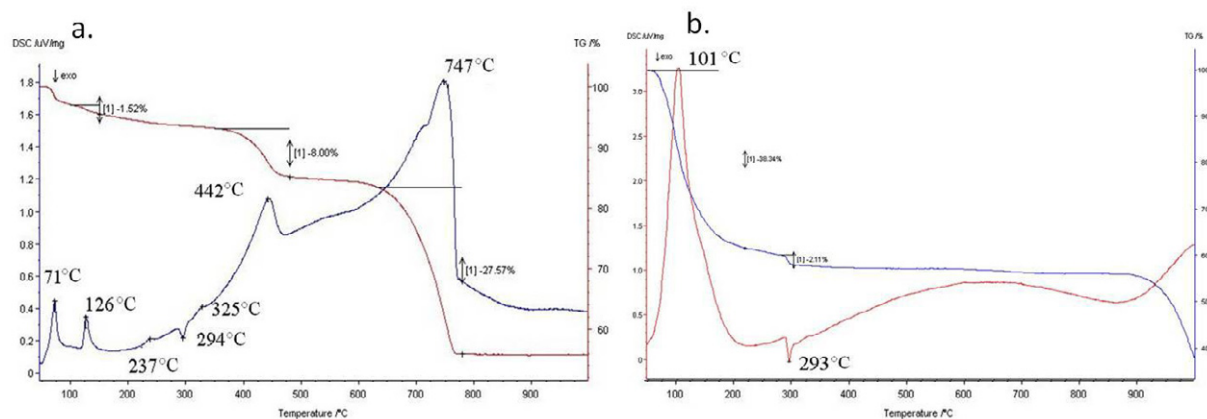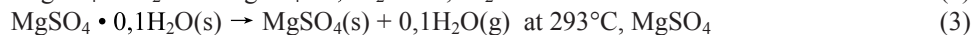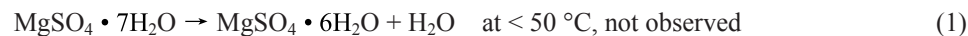

Fig. 4 TG-DSC analysis: (a) sample 4 from the finishing layer; (b) sample S1 salt efflorescence

Table 2 Summary of the chemical compounds present in the stuccoes; the relative percentages were calculated from TG-DSC analysis and reported when available

Sample	Layer	Water (%)	Hydromagnesite (%)	Gypsum (%)	MgCO$_3$ (%)	CaCO$_3$ (%)	Epsomite (%)
4	Surface layer	2,4	traces	14,5	15,3	70,4	traces
8	Bulk	0,6	-	4,4	7,0	73,4	-
S1	Salt efflorescence	38,3	-	-	-	-	82,4
11	Finishing layer	^	-	X	X	X	-
15A	Finishing layer	^	-	X	X	X	-
15Bs	Finishing layer	^	-	X	X	X	-
15B b	Bulk	^	-	X	X	X	-
15B e	Salt efflorescence	^	-	-	-	-	X

X= compound present; - = compound not present; ^= not detected

4. Conclusions

The chemical-physical study of the stucco samples of the Addolorata Chapel allowed to obtain interesting information about the composition of the stucco and the techniques used in the 17th century in Venice. The

preparation of degradation maps gave important information for verifying the conservation state of the surfaces (e.g. efflorescence, detachments, etc.) and for proceeding to a representative sampling.

Combining the results of the different analysis (Table 2), the composition of the stuccoes was identified and two different layers were recognized: a bulk material covered by a brighter and smoother finishing layer.

Both gypsum and calcium hydroxide were detected as binders in all the samples confirming the use of stucco forte. Quartzitic sand and carbonatic aggregates where used in the bulk material, while only calcium carbonate (probably marble powder) was found in the surface layers.

Interesting, in comparison to the traditional *stucco forte* receipt, is the presence of hydromagnesite and magnesite in the stucco. Magnesite usually does not develop within the normal carbonation processes from magnesium hydroxide. While at room temperatures the formation of various metastable hydrous magnesium carbonates, as hydromagnesite, often occurred, high temperatures (100 °C) are required for the formation of the magnesium carbonate [16]. Therefore, the presence of magnesium carbonate is probably due to the use of magnesite, while the low amount of hydromagnesite detected might derive from the presence of brucite $Mg(OH)_2$ present in the original binder, probably produced partly from a dolomitic stone.

The presence of magnesite aggregates might be related to an intentional addition for improving the workability of the stucco mixture. Magnesite aggregates work as modifier of the crystalline structure of gypsum extending its setting time [17; 18].

The presence of magnesite rather than hydromagnesite agrees with other examples of "stucco forte" in Venice between the 16th and 17th century [1; 19], confirming moreover the use of this peculiar mixing of gypsum, calcium hydroxide, marble powders, silicatic sands, and magnesite aggregates in Venice.

The bad conservation state of the decorations was due to the formation of salt efflorescences, in particular epsomite, that caused decohesion and disaggregation processes. The epsomite formation is probably related to water percolating from the roof and consequent solubilization of sulphate ions that react with magnesium ions present in the matrix.

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