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STUDY BY THERMAL ANALYSIS OF MORTARS BELONGING TO WALL PAINTINGS CORRESPONDING TO SOME HISTORICAL BUILDINGS OF SEVILLIAN ART

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Mortars taken from the walls of three historical buildings in Seville: Pond of Patio de las Doncellas in Real Alcazar of Seville, the Monastery of Santa Maria de las Cuevas and the Church of El Salvador were investigated.

The techniques employed were thermogravimetry (TG), differential thermal analysis (DTA), XRD, FTIR, SEM with EDAX, Bernard calcimeter, granulometry, mercury intrusion porosimetry and mechanical strength tests.

The majority of the studied mortars consist of calcite and silica. Gypsum was detected in samples of four mortars from the Santa Maria de las Cuevas Monastery and two from the El Salvador Church, whose samples were taken from the upper layers of the walls, but gypsum was not detected in the internal mortars layers. Only in two of the samples of the Monastery, the presence of cellulosic material as an organic additive was detected.

All the studied mortars could be regarded hydraulic, so much by results from ratios between mass loss due to CO_2 and H_2O, hydraulic module and assays of compressive strength. The values obtained by these three techniques are related, providing good agreements between them.

These results give useful information that aids in understanding the technology of historic mortars, and how to plan the restoration of these wall paintings.

Keywords: *calcite, FTIR, historical buildings, SEM, silica, thermal analysis, XRD*

Introduction

Traditionally, mortars are composite materials whose structural properties are due to the mixture of silica or carbonate sand with a binder fraction [1–5]. Depending on clay percentages in addition to calcium and magnesium carbonates, binders are defined as aerial or hydraulic, as it hardens in presence of water [6].

The binders contribute workability and elasticity to the mortars while the aggregate contributes to mechanical properties, acts as filler and controls problems arising from shrinkage.

Recently, raw material composition, as well as the physical, mineralogical and microstructural characteristics of mortar samples from some historic buildings were determined to understand their technology and to produce compatible repair mortars with the existing ones in masonry structures [7–9]. The criteria of intervention, reinstatement and re-growth with mortar or another type of material, with progressively plastic properties, suggest several reasons like the adequacy to the adjacent environment, or that the material is the most similar thing to the stony support with regard to its mechanical resistance and porosity. In addition, it is important to eliminate harmful substances from the stony support such as: soluble salts, acidic material, and alkalis [9].

The DTA-TG techniques provides a very good understanding of the thermal behaviour of mortars, showing different temperature regions, which decomposition processes are carried out [3–5].

Wall painting may be defined as any painted design or composition applied directly to the surface of a building. Ranging from simple decorative patterns to more complex figurative or even narrative schemes, wall paintings form integral components of the monument [10].

There are few studies about the mortars that serve as support for wall paintings. The aim of this work is to comparatively study the mortars components belonging to wall paintings in historical buildings of Sevillian art: the Santa Maria de las Cuevas Monastery (baroque style, mortars from XVI and XVII centuries), El Salvador Church (baroque style, mortars from XVIII century) and Real Alcazar of Seville (Mudejar style, mortars from XV–XVI centuries).

The wall facing the central pond of the Patio de las Doncellas del Palacio Mudejar del Rey Pedro I de

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Castilla in Real Alcazar of Seville had a lining of lime mortar embellished with an ornamental finish and a geometric drawing of Mudejar bow manufacture. The Patio was built in 1356. Between the end of the XV century and the middle of XVI century a new lime mortar was applied on top of the original surface and decorated with waves of colour in several arrays, alternating very light yellow and blue [11–14]. The Santa Maria de las Cuevas Monastery, located on an island near the centre of Seville, was considered one of the most important cultural centres (paintings, sculptures, wall paintings, metals, etc.) from 1400 to 1836, when monks were removed. The construction of El Salvador Church took place from 1674 to 1712, the last period of the work being lead by the architect Leonardo de Figueroa. Inside the church there are artworks from Martinez Montańes and Juan de Mesa as well as priceless wall paintings in the Dressing Room of Virgen de las Aguas. Presently, the Church enmeshed in the laborious process of complete restoration [15, 16].

Experimental

Sampling

A list of the samples taken from the ancient walls of the Central pond, Monastery and Church is reported in Table 1. Two types of samples were collected from the central pond of Real Alcazar; in order to examine the differences between the two historical mortars. In all cases, the extracted samples contained both the paintings and the mortars that serve as support.

Methods

Thermal Analysis estimates the amounts of the binder fraction. DSC and TG measurements were performed by means of a SDT Q600 simultaneous analyser. X-ray diffraction clarifies the nature of the mineralogical phases present in the sample. X-ray diffraction investigations were perfomed using a Siemens diffractometer model Kristallofex D-5000. FTIR points out the nature of the binder fraction, salts, and decay products eventually present in the mortars. Fourier Transform Infrared spectra were taken by a Nicolet 510 with an incorporated microscopy spectrometer covering the 400–4000 cm^{-1} range. With the aim of carrying out quantitative estimation of the amounts of calcite and silicates, we applied classical methods such as Bernard calcimeter and granulometry. A scanning electron microscope (Jeol JSM5400) equipped with an X-ray microprobe allowed morphological and elemental investigation. X-rays fluorescence measurements were carried out by an XRF espectrometer Siemens SRS-3000.

Additional structural information may come from porosimetric analyses, and other techniques, such as mercury intrusion porosimetry (the porosity of the samples was evaluated by calculating the total area of the distribution curve obtained by a mercury Quantachrome Poremaster porosimeter) and mechanical strength tests (Mechanical properties of strenght and hardness were carried out using a Form+Test Seidner Prüfmashinen U. Laborgeräte Type 505/200/10DM1), elucidated physico-chemical characteristics [1].

Table 1 List of the samples of mortars taken from walls of the three historical buildings studied

a/a	Code number	Century	Location
1	66	XV–XVI	Pond of Patio de las Doncellas, Real Alcazar
2	115	XVI	Pond of Patio de las Doncellas, Real Alcazar
3	116	XV–XVI	Pond of Patio de las Doncellas, Real Alcazar
4	114	XVI	Pond of Patio de las Doncellas, Real Alcazar
5	M (upper and internal)	XVI–XVII	Prebistery of Principal Room, Monastery
6	N	XVI–XVII	Prebistery of Principal Room, Monastery
7	D	XVI–XVII	Ornament of Principal Room, Monastery
8	K (upper and internal)	XVI–XVII	Ornament of Principal Room, Monastery
9	L (upper and internal)	XVI–XVII	Central Room, Monastery
10	B	XVI–XVII	Dining Hall, Monastery
11	A (upper and internal)	XVI–XVII	Dining Hall, Monastery
12	CS1	XVIII	Column of the Pulpit, El Salvador Church
13	CS2	XVIII	Column of the Pulpit, El Salvador Church
14	RES (upper and internal)	XVIII	Gospell Altarpiece, El Salvador Church
15	OS (upper and internal)	XVIII	Oratory Dressing Room Virgen Aguas, El Salvador Church

Results and discussion

Thermal analysis and X-ray fluorescence studies

Thermal analysis allowed an adequate characterization of mortars used in cultural heritage [3–5]. The curves of TG and DTA showed some significant temperature regions, corresponding to thermal decomposition mechanisms, which have been used to characterize the kind of mortars used in the construction. Also, thermal analysis and compositional characterization by X-ray fluorescence were carried out in order to evaluate the hydraulic properties of mortars.

Relations between mass loss due to CO_2 (mass loss due to the carbon dioxide content of the carbonated lime between 600 and 900°C) and H_2O (mass loss due to chemically bound water of hydraulic products between 200 and 600°C) were made following TG graphs of different samples. The CO_2/H_2O ratios were found to be less than 10 in all the samples (in upper samples, part of the internal layer of the mortars was taken) (Table 2). This one means that all mortars could be regarded as hydraulic, and that they offer good mechanical properties.

The mortars were also characterized by X-ray fluorescence and the percent of compounds such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O and Na_2O were obtained (Table 3). Hydraulic character was related to the hydraulic module, which is defined by the following equation [6]:

$$\text{H.M.} = (\%\ CaO + \%\ MgO + \%\ K_2O + \%\ Na_2O)/ /(\%\ Al_2O_3 + \%\ SiO_2 + \%\ Fe_2O_3) \quad (1)$$

The ideal value of hydraulic module in order to obtain high resistance must be between 1.8 and 2.2. When the value is lower than 1.8 very low resistance is obtained and cracking take place, while values greater than 2.2 are due to a high content of CaO, which produces an excess amount of free CaO [17].

Mortars that gave results near to ideal values were M_{int} (1.69), K_{int} (2.34), A_{int} (2.33), and also, belonging to Virgen de las Aguas Monastery, mortars N (2.24) and L_{int} (2.21). Other mortars that gave good results in this subject were CS1 (1.79) (El Salvador Church), and 66 (1.91) and 114 (2.23) belonging to Real Alcazar. These results show compatibility between results from TG and from other techniques such as X-ray fluorescence.

In some samples, the results of bulk (internal layers) measured by ATD/TG did not agree with results obtained by XRD, IR and XRF techniques. Figure 1 shows thermal curves of the samples A_{upper}, M_{upper}, N, L, K_{upper} from Santa Maria de las Cuevas Monastery or 115 from Real Alcazar. An endothermic

Table 2 Relations between mass loss due to CO_2 and H_2O following thermal analysis data, and measurements of compressive strength

	Mortars	CO_2/%	H_2O/%	CO_2/H_2O	Comprehensive strength/MPa
Real Alcazar	66	32.82	5.33	6.16	–
	115	19.10	5.21	3.66	–
	116	–	–	–	–
	114	30.84	5.87	5.25	–
Santa Maria de las Cuevas Monastery	M_{upper}	9.49	2.58	3.68	4.86
	M_{int}	26.31	5.21	5.05	10.15
	N	27.02	3.60	7.50	9.55
	D	24.80	5.47	4.53	12.35
	K_{upper}	4.62	1.41	3.28	3.97
	K_{int}	24.92	4.95	5.03	9.77
	L_{upper}	8.47	2.00	4.23	3.06
	L_{int}	25.15	5.53	4.55	9.64
	B	–	–	–	–
	A_{upper}	2.78	1.42	1.95	3.75
	A_{int}	27.01	6.02	4.49	10.44
El Salvador Church	CS1	27.04	3.90	6.80	9.10
	CS2	–	–	–	–
	RES_{upper}	17.50	5.95	2.94	3.50
	RES_{int}	31.50	5.96	5.27	10.12
	OS	–	–	–	–

Table 3 Percent of compounds SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O and Na_2O by X-rays fluorescence, and hydraulic module calculated for each mortar

	Mortars	SiO_2/%	Al_2O_3/%	Fe_2O_3/%	CaO/%	MgO/%	K_2O/%	Na_2O/%	M.H.
Real Alcazar	66	25.00	3.70	0.68	55.00	0.03	1.12	0.02	1.91
	115	38.00	3.40	0.71	45.40	0.02	0.53	0.03	1.09
	116	32.40	3.20	0.70	48.80	0.02	0.19	0.03	1.36
	114	23.00	3.11	0.45	58.12	0.03	1.12	0.02	2.23
Santa Maria de las Cuevas Monastery	M_{int}	21.97	3.61	0.92	39.51	1.61	0.84	0.29	1.69
	N	26.51	3.26	0.63	65.38	1.28	1.04	0.33	2.24
	D	31.83	3.54	1.04	58.50	1.57	1.17	0.49	1.69
	K_{int}	25.13	2.97	0.62	67.48	1.64	0.68	0.25	2.34
	L_{int}	20.99	3.18	0.70	52.41	1.50	0.74	0.21	2.21
	B	11.58	1.69	1.17	80.79	1.19	0.30	0.40	5.73
	A_{int}	17.01	2.92	0.63	44.11	3.11	0.47	0.14	2.33
El Salvador Church	CS1	33.89	1.47	0.26	62.67	0.90	0.22	0.16	1.79
	CS2	13.46	1.62	0.18	82.50	1.05	0.26	0.26	5.51
	RES_{int}	12.59	1.24	0.16	49.37	1.24	0.62	0.64	3.84
	OS_{int}	10.67	1.31	0.14	42.27	1.50	0.37	0.42	3.68

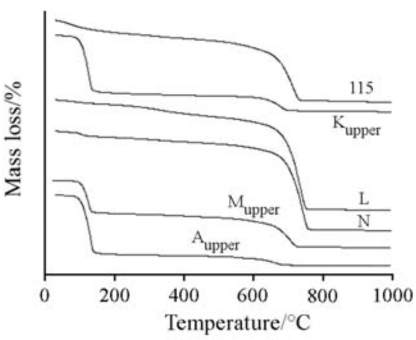

Fig. 1 TG thermal curves of the samples A_{upper}, M_{upper}, N, L, K_{upper} and 115

peak due to gypsum dehydration (100–150°C) is detected in samples taken in the upper layers of the mortars A, M and K (also, in these samples, part of internal layer was collected together the upper one). In XRD and XRF measurements of the bulk there is no evidence of gypsum. The detection of gypsum by thermal study may be attributed to the samples obtained from upper layers of the wall, where polychrome plastering was observed.

X-ray diffraction, Bernard's calcimeter, SEM and IR studies

X-ray diffraction studies showed that the majority of the mortars are constituted mainly by calcite and silica. Four mortars from Santa Maria de las Cuevas Monastery (N, D, K and B), two from El Salvador Church (CS1 and CS2) and two from Real Alcazar (66 and 116) showed a very high content of calcite (Fig. 2a). The values obtained are typical of mortars rich in lime and/or due to the presence of carbonated sand.

Nevertheless, the presence of a high quantity of gypsum has been detected in three mortars (M, L and A) of Santa Maria de las Cuevas Monastery, and two mortars (RES and OS) of El Salvador Church (Fig. 2b). The samples belonging to these last mortars were taken in the upper layers of the walls (M_{upper}, L_{upper}, A_{upper}, RES_{upper} and OS_{upper}). Also, in these mortars, bulk samples from the internal layer were collected (M_{int}, L_{int}, A_{int}, RES_{int} and OS_{int}).

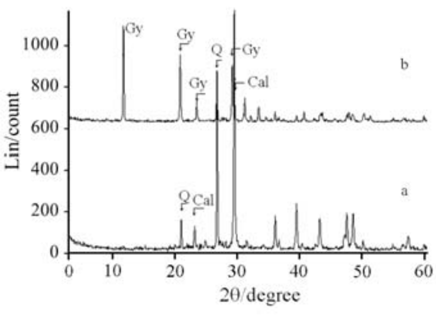

Fig. 2 a – XRD of mortars N and b – L_{upper} (*Gy*=gypsum; *Q*=quartz; *Cal*=calcite)

Semiquantitative results obtained by X-ray diffraction agreed with those obtained by Bernard's calcimeter [16] (Table 4).

Likewise, FTIR and EDX results are in good agreement with XRD and Bernard's calcimeter. FTIR analysis gave information about the presence of characteristic atom groups of $CO_3^=$ (carbonates) (1450, 875, 1797 cm^{-1}), $SO_4^=$ (sulphates) (3550, 3405, 1130, 670, 602 cm^{-1}) or SiO_4^- (silicates and quartz) (1200–900, 500–400 cm^{-1}) in the different mortars. Figure 3a shows IR spectra of mortar L (L_{upper}) [16].

The results of bulk (internal layers) of some samples measured by XRD, IR and XRF did not agree with results obtained by ATD/TG. The detection of gypsum by thermal techniques may be attributed to the samples obtained from upper layers of the wall.

To check the differences between results obtained by ATD/TG, XRD and XRF techniques, samples (A, M, K, RES and OS) taken from internal layers were studied by DTA/TG and XRD and did not show the presence of sulphates.

Fibers were detected by optical microscopy in the fraction >200 μm of three samples (B, L and K) of Santa Maria de las Cuevas Monastery (figure not shown). The presence of fibers was confirmed by infrared spectroscopy, appearing the typical bands of cellulose, hemicellulose, pectin and lignin. In this form, the band at 1735 cm^{-1} was assigned to group C=O belonging to pectin; bands at 1595 and 1505 cm^{-1} were assigned to aromatic vibrations of lignin; bands of polysaccharides (C–C vibrations of the ring at 1155 cm^{-1} and glycosidic bound C–O–C at 1105 cm^{-1}); two bands at 2800–2950 cm^{-1} were assigned to CH_2 and CH_3 groups attributed to organic material (Fig. 3b). In general, the use of this type of materials provided major elastic qualities to the mortars and avoided possible cracking [16, 18].

From morphological point of view, all the samples were studied by scanning electron microscopy. Gypsum crystals from sample M_{upper} were photographed as well as crystals of calcite proceeding samples B and 115 or grains of quartz belonging to samples 66 or D. The photomicrographs are shown in Figs 4a, b and c. In the different mortars studied,

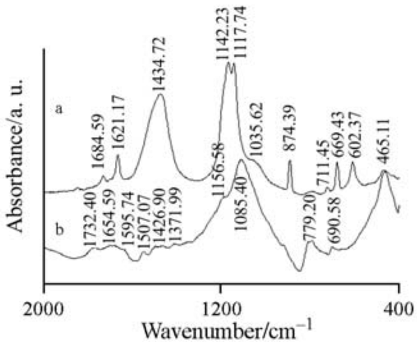

Fig. 3 a – IR spectrum of mortar L (L_{upper}) showing bands corresponding to calcium carbonate, gypsum and quartz; b – IR spectrum of fraction >200 μm of mortar K (K_{int}) showing bands corresponding to silicates and cellulosic fibers

Table 4 Semiquantitative results by X-ray diffractions and Bernard's calcimeter results of all mortars

Building	Mortars	Calcite/%		Quartz/%	Gypsum/%
		Bernard's calcimeter	XRD	XRD	XRD
Real Alcazar	66	78.09	78	22	0
	115	–	–	–	–
	116	63.81	74	26	0
	114	–	–	–	–
Santa Maria de las Cuevas Monastery	M_{upper}	8.76	20	20	60
	N	61.99	80	20	0
	D	58.08	67	33	0
	K	60.06	80	18	2
	L_{upper}	32.68	42	11	47
	B	70.04	90	10	0
	A_{upper}	6.78	3	42	55
El Salvador Church	CS1	59.08	51	39	0
	CS2	78.83	92	8	0
	RES_{upper}	33.77	43	9	48
	OS_{upper}	31.46	38	14	46

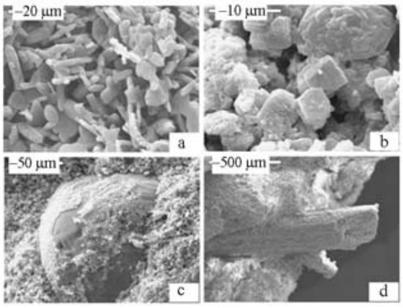

Fig. 4 Scanning electron microscopy micrographs of a – crystals of gypsum of sample M (M_{upper}), b – crystals of calcite of sample 115, c – grains of quartz of sample 66, d – straw and fibers of mortar K (K_{int})

observations at different magnitudes showed differentiation in the size between gypsum and calcite grains ranging between 10–20 and 3–7 µm respectively. Also, straw and other fibers were detected in analysis of mortars B and K by scanning electron microscopy (Fig. 4d).

Study of physical properties

The compressive strength values of almost all mortars were found to be higher than 10 MPa (Table 2). Considering the compressive strength values of more than 9 MPa for hydraulic mortars in the relevant literature, the samples may also be accepted as hydraulic mortars [19, 20]. These results are in agreement with those obtained by DTA-TG, CO_2/H_2O ratio, and hydraulic module.

Lastly, the porosimetric test revealed in almost all samples, the presence of a large percentage of macro pores (0.05–1 µm) according to IUPAC classification. The total porosity of samples varied between 11 and 53% depending on monument studied. Values of porosity in mortars of Santa Maria de las Cuevas Monastery showed a high range of percentages; the lowest value corresponding to mortar D (15.42%) and the highest value corresponded to mortar K_{int} (52.76%). Mortars belonging to Real Alcazar showed lower values than the average of Monastery mortars, 11.89% in mortar 116, 13.03% in mortar 66, 25.33% in mortar 115 and 28.70% in mortar 114.

Conclusions

Mortars taken from the Pond of Patio de las Doncellas in Real Alcazar of Seville, the Monastery of Santa Maria de las Cuevas and the Church of El Salvador were investigated. Thermal studies provided a very good characterization of the thermal properties of the mortars, which were used to distinguish between the different types of the same ones that are used in cultural heritage.

All the studied mortars could be regarded hydraulic, so much by results from TG (relations between mass loss due to CO_2 and H_2O), XRF (hydraulic module) and assays of compressive strength. The values obtained by these three techniques are related, providing good agreements between them.

X-ray diffraction studies showed that the majority of the mortars consist of calcite and silica. Only mortars M, L and A, which belong to Virgen de las Cuevas Monastery and the mortars RES and OS of El Salvador Church, present a high content of gypsum, placed principally in upper layers, and is assigned to the presence of polychrome plastering. The rest of the mortars are very rich in calcite.

The homogeneity in porosity values was major in mortars belonging to Real Alcazar compared to those from the Monastery or from the Church.

These results give useful information that aids in understanding the technology of historic mortars, and how to plan the restoration of these wall paintings.

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