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MICROSCOPIC CHARACTERISATION OF OLD MORTARS FROM THE SANTA MARIA CHURCH IN ÉVORA

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Abstract

Evora Cathedral is one of the most emblematic monuments of Evora (Portugal) and is classified by UNESCO as a World Heritage site.

This monument has suffered several conservation and restoration interventions through the ages, without, however, any type of previous knowlegde about the type of mortars and materials used. This work was carried out in order to identify the mortar's composition in different places, which were attributed to different construction or conservation periods.

The characterization methodology involved a multidisciplinary set of chemical, physical, microstructural and mechanical techniques, and gave special attention to the use of microstructural characterization techniques, particularly petrographical analysis and scanning electron microscopy for the identification of the mortar's constituents as well as in the evaluation of the state of conservation.

The test results showed that two types of aerial binders were used, dolomitic lime and calcitic lime, the former being predominant The aggregates used have a siliceous nature and are similar in composition to the granodiorites of Evora's region. The mortars differ in the proportion of aggregates and, in some cases, crushed bricks were used as an additive.

Keywords: SEM, petrographical charactization, old mortars.

Introduction

The Santa Maria Church of Evora (Evora's Cathedral) (see figure 1) is one of the most important monuments in Evora, a Southern Portugal monumental town classified by UNESCO as World Heritage. The Cathedral has a Romanic-Gothic style, or Gothic with Cistercian and Medicant influences, where it is possible to observe a diversity of transition construction solutions that were employed.

The construction of the actual Cathedral dates back to the 13th century and was inspired in the model of Lisbon's Cathedral and foreign cathedrals. The main architects or masters were Domingues Pires, between 1280 and 1303, and Martim Domingues, responsible for finishing the construction in 1304 and 1334 and the contruction of the cloister and the portico of the main entrance.

The Evora's cathedral is a monumental complex composed by the church itself and the cloister. Figure 2 shows the south view of the monument with the identification of some important features namely the zimborium (the top of the dome), the two towers over the main façade – the Tiled Tower (*torre dos azulejos*) and the Clock Tower (*torre do relógio*), the rose window in the south side of the transept and the most recent part of the Church, the Main Chapel. With exception to the Main Chapel which was built with white marbles from Estremoz (a town 40 km Northeast of Evora), the whole monumental complex was built with materials of granitoid composition, namely granite, granodiorite and gneiss. Inside the church, it is difficult to assess the lithological nature of the materials used, due to the existence of a thick render covering almost all the walls and columns (Costa and Rodrigues, 2000).

The present work is the result of a joint collaboration between the National Laboratory of Civil Engineering (LNEC), the University of Evora and the Portuguese Institute of Architectural Heritage (IPPAR) aimed at the development of integrated conservation strategies for important religious buildings from Southern Portugal (project CATHEDRAL - POCI/HEC/57915/2004). The main goal is to undertake the characterization of ancient mortars giving valuable information about a monument's history, namely the techniques of construction, past interventions and degradation processes and allowing the evaluation of the mortars macrostructural and microstructural properties which are essential parameters for the design of new aesthetic and functional compatible restoration mortars.

Figure 1: Main façade of Evora's Cathedral.

Figure 2: Aerial view of Evora's Cathedral – church and cloister.

Sampling methodology

The sampling of mortars is a crucial step that can influence the success of the characterization methodology, as has been pointed out by several studies (Chiari et al, 1996; Hughes et al, 1999, Veiga et al, 2001, Candeias et al, 2006). The selection of the sampling sites was made with the help of IPPAR technicians. The size of each sample was the minimum that could guarantee the success of the analysis and the confirmation for future studies. Seven mortars were sampled from different sites, according to IPPAR recommendations, as shown in the figure 3 and described in table1.

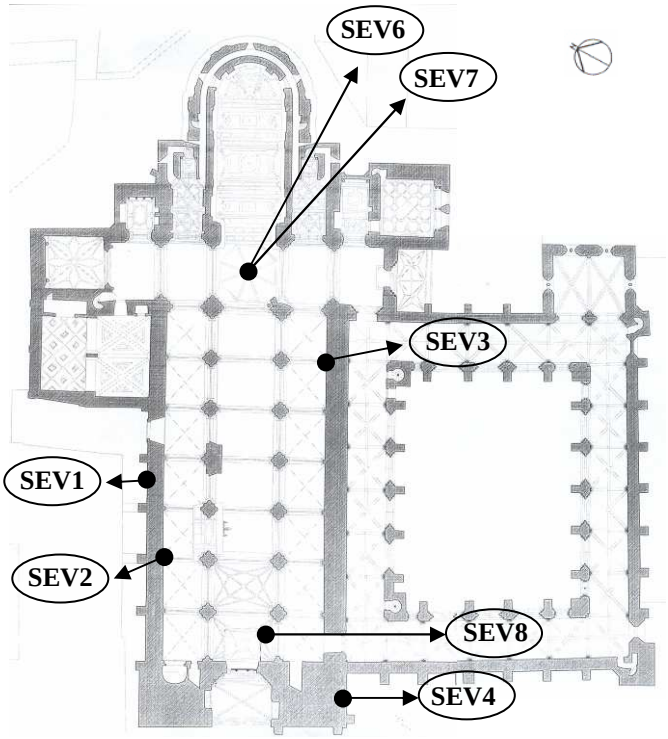

Figure 3: Plan of Evora's Cathedral and sampling sites.

Table 1: Description of the ancient mortar samples

Sample	Mortar function	Probable date (century) (Wevers, 2004)	Location
SEV1	render	XVII	Exterior of the cathedral – terrace
SEV2	render	XIV	North side nave (Pillar 2)
SEV3	render	XIII	South side nave (Pillar 25)
SEV4	render	XVI	Inside of the window arch of the *torre lanterna*
SEV6	Filler mortar	XIV	Inner wall of the Zimborium Tower
SEV7	Filler mortar	XIV	Inner wall of the Zimborium Tower
SEV8	render	XVI	High choir (behind wooden chair structure)

Figure 4 shows details of the collected mortar samples. Preliminary observation showed that samples SEV1, SEV2 and SEV4 are composed by only one layer with thicknesses of 30, 20 and 15 mm, respectively. All samples showed high mechanical resistance and adhesion to the substrate and small nodules of lime. The samples SEV2 and SEV4 showed ceramics fragments.

Observation of sample SEV3 with the naked eye allowed the identification of three distinct layers: – one inner layer (closest to the masonry) with beige color, low mechanical resistance and with a large grain size distribution, designated SEV3-INT; an intermediate layer with 10 mm thickness, lighter color than the previous layer occasionally slightly pink, more resistant and with small ceramic fragments, designated as intermediate SEV3-IM; and an outer layer with 2 mm thickness, dark brown color, high mechanical resistance and adhesion to the substrate, refered as SEV3-EXT.

Samples SEV6 and SEV7, both taken from inside the Zimborium walls, are composed of only one layer with about 15 mm of thickness, light brown color and low mechanical resistance. Sample SEV7 showed the presence of lime nodules with larger dimensions and had a gray lime washing with a rough finishing.

Observation of sample SEV8 allowed the identification of four layers: - one inner layer of beige color with 15 mm thickness and low mechanical resistance. This layer was designated as SEV8-INT. A render layer with dark brown color, with 1mm tickness and high resistance and adhesion, designated by SEV8-EXT; and two limewashing paint layers, one gray and another white. Ceramic fragments and lime nodules of small dimensions were observed in layer SEV8-INT.

Figure 4: Detail of the collected mortar samples.

Characterization methodology

The mortars were thoroughly examined in the laboratory using an Olympus stereo-zoom microscope and carefully disaggregated to avoid breaking the existing aggregates.

Scanning electron microscopy observations were performed on a JEOL JSM-6400 Scanning Electron Microscope (SEM) coupled with a OXFORD Energy Dispersive Spectrometer (EDS) Si(Li) X-ray detector.

X-ray diffraction (XRD) was carried out with a Phillips diffractometer with Co Kα radiation, speed of 0.05 º/s and 2θ ranging from 3 to 74. Two types of fractions were analysed, the fraction corresponding to the mortar as collected, designated as *overall fraction* and obtained by grinding the disaggregated mortar to pass in a 106 μm sieve and a fraction designated as *fine fraction*, which has a higher binder concentration and was obtained from the fines of the disaggregated material passing a 106 μm sieve. The overall fraction of each sample was also used for thermal analysis (TGA-DTA) performed in a SETARAM TGA-DTA analyser, under argon atmosphere, with heating rate of 10°C/min, from room temperature to 1000°C.

Thin sections and polished surfaces of the mortars were prepared by vacuum impregnation with an epoxy resin. These were observed with a Nikon petrographic microscope and images were recorded digitally.

For the chemical analysis of the binder components, small portions of the mortars were carefully disaggregated and all types of impurities and limestone grains were separated. Samples were afterwards digested in warm dilute hydrochloric acid (1:3) to separate the siliceous aggregates from the lime paste. For the soluble fraction, the amounts of calcium, magnesium, aluminum, iron and sodium (expressed in terms of their oxides) were determined by atomic absorption spectrometry, chloride ion was determined by potentiometry and sulphate ion was determined by gravimetry. The insoluble residue was weighed and sieved to determine the particle size distribution of the aggregate fraction *i.e.* the siliceous sand.

All mortars were dried at 40ºC for at least 12 hours, with exception of the samples for chemical analysis, which were dried at 105ºC.

Results and discussion

Optical microscopy

Preliminary observation of the samples and of polished surfaces (figure 5) under a stereomicroscope showed that all mortars contain round nodules of lime which may indicate that the lime was slaked with a minimum amount of water to convert CaO into $Ca(OH)_2$ (Schouenborg, 1993; Elsen, 2004).

All samples, with exception of SEV6 and SEV7, presented a binder with brown color. The samples were heterogeneous and the aggregates showed different color, nature and size. Round nodules of lime and ceramics fragments were observed in all samples with exception ot the samples from the Zimborium tower (SEV6 and SEV7).

Observation of thin-sections under a petrographic microscope allowed a further insight into the mortars composition. Thin-sections from samples SEV1, SEV2 and SEV4 were analysed (figure 6). The first two samples proved to be almost identical and showed a binder composed mainly by a carbonate phase with higher amount of neoformation calcosilicates than SEV4 sample. It was possible to observe microcrystalline phases of silica. The most part of the aggregates are clastic materials from the disaggregation of granodiorite rocks. Sample SEV1 presented two distinct features, a high abundance of neoformation calcossilicates dispersed in the matrix, at aggregate-binder interfaces and fractures, and the presence of appreciable amounts of olivine. The presence of olivine which is highly susceptible to meteorization demonstrates the minimal transport of the aggregates thus corroborating the results that indicated that these were produced from crushed/dissagregated rocks. Moreover, it allowed the identification of the aggregates possible provenance because the only identifiable local source of rocks with this type of minerals is the *Alto de S. Bento* quarry area, in the vicinity of Evora, which is composed of granodiorite rocks with gabro inclusions. The formation of calcossilicates in the binder was also detected, consequence of the pozzolanic reactions between the binder and siliceous pozzolanic materials, like the ceramics. The presence of these neoformation compounds explains the good mechanical properties of these mortars (Adriano et al, 2006).

The dominant clasts on sample SEV4 are also typical granodiorite/granite constituints: quartz, feldspars (plagioclasis included), biotite and muscovite. The mineralogical composition and the shape of the aggregates (fairly angular) suggest that the transport was small thus corroborating the previous observations. It was also possible to detect minor quantities of lime nodules not absorved into the mortar, ceramic fragments essentially composed of calcossilicates that link the quartz clasts and the rare muscovite grains. It was observed two differents kinds of amphiboles: horneblende and a green and fibrous amphibole and crystalline epidote agglomerate (figura 6d).

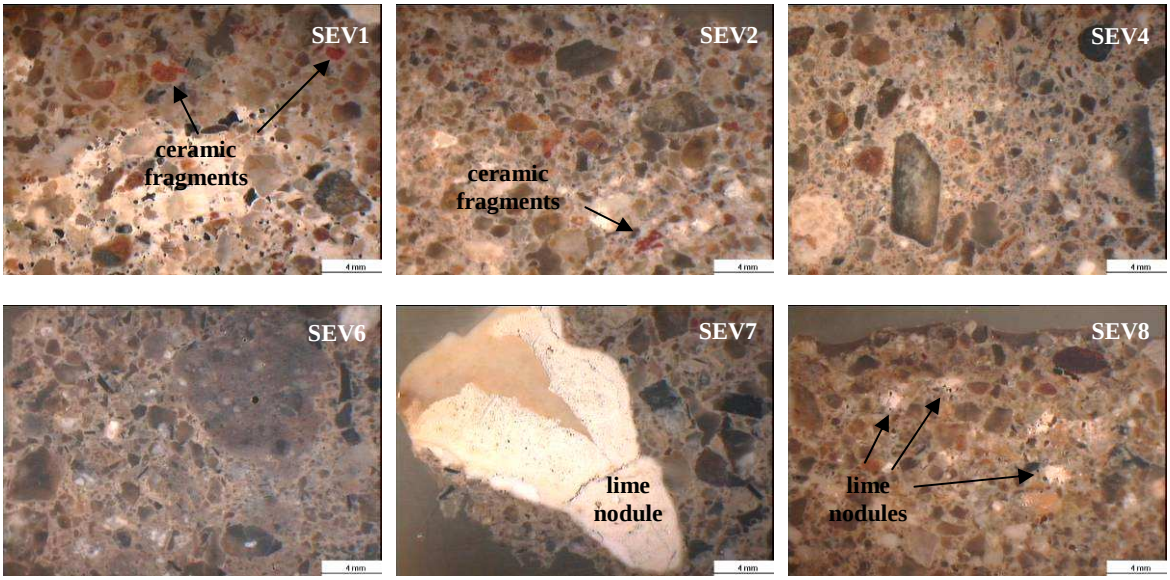

Figure 5: Observation of polished sections mortars at stereomicroscope showing crushed ceramics, lime nodules and siliceous aggregates.

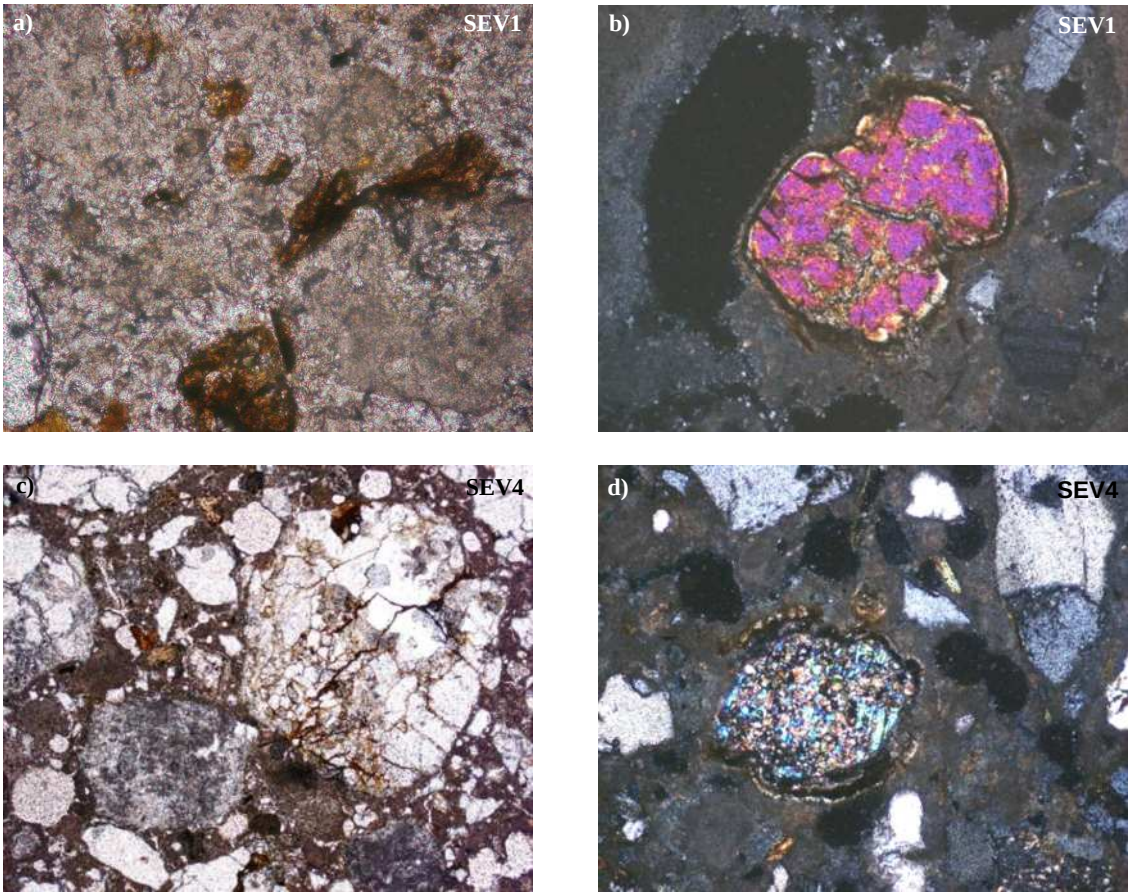

Figure 6: Thin-sections observation of the mortars. a) carbonated-siliceous matrix with neoformation calcosilicate agglomerates (120x) in plane polarized light; b) olivine crystal (30x) in crossed polars; c) neoformation calcosilicate bands growing in fractures and aggregates-binder interfaces (12x) in plane polarized light; d) epidote cristals (30x) in crossed polars

XRD Analysis

Table 2 presents the mineralogical composition of the overall fraction of the mortars determined by XRD analysis.

The results show that the mortars are essentially composed of carbonates (calcite, aragonite, dolomite, hydromagnesite and magnesite) and siliceous aggregates corroborating the previous observations. The presence of soluble salts, halite and gypsum, is normally an indicator of the occurrence of chemical degradation phenomena in the mortars.

The most striking feature is the nature of the binder which allows distinction of the studied mortar samples. Samples SEV6 and SEV7 have essentially calcite which indicates that it is a calcitic lime while the other samples possess calcium and magnesium carbonates which indicate that dolomitic materials were used to produce the aerial lime for these mortars.

Table2: Mineralogical composition of the mortars assessed by XRD

Crystalline phases	SEV1	SEV2	SEV3			SEV4	SEV6	SEV7	SEV8	
			INT	IM	EXT				INT	EXT
Quartz	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Feldspar	+/++	++	++	++	++	++	++	+/++	++	++
Mica	+	+	+/++	+/++	+/++	+/++	+/++	+++	+	+
Chlorite	-	-	vtg/?	?/vtg	?/vtg	+	vtg	+	-	vtg
Amphiboles	vtg/+	vtg	vtg/+	vtg/+	vtg/+	vtg/+	-	-	vtg/+	vtg/+
Zeolitic mineral	vtg	vtg	-	-	-	vtg	-	-	-	-
Halite	-	vtg	-	-	-	?	-	-	vtg	-
Kaolinite	-	-	-	-	-	?/vtg	-	-	-	?
Calcite	++	+/++	++	++	++	++	++	+	+/++	+/++
Magnesite	vtg	vtg	+	+	+	+	-	-	vtg	vtg
Dolomite	?/vtg	vtg	-	-	-	vtg	-	-	vtg	vtg
Hydromagnesite	+	vtg	-	-	-	?/vtg	-	-	vtg	+
Aragonite	-	vtg/+	-	-	-	-	-	-	-	-
Olivine	-	?/vtg	-	-	-	-	-	-	-	-
Mulite	-	-	-	-	-	-	-	-	-	-
Gypsum	-	-	-	-	-	-	-	-	vtg	vtg
Brucite	-	-	-	-	-	-	-	-	-	vtg

+++ abundant, ++ present, + small amount, vtg traces, - undetected

Thermal Analysis

The thermograms of all samples are typical of aerial lime mortars of dolomitic/calcitic nature, with exception of samples SEV6 and SEV7 that present thermograms typical of calcitic aerial mortars with an important weight loss for temperatures ranging between 550 and 900°C.

In some mortars (SEV1, SEV2, SEV4 and SEV8) the presence of hydromagnesite was identified (figure 7). The hydromagnesite decomposition can be represented by the following equations (Bruni et al, 1998).

$$4MgCO_3(s)\cdot Mg(OH)_2(s)\cdot 4H_2O(l) \rightarrow 4MgCO_3\cdot Mg(OH)_2(s) + 4H_2O(l) \quad (1)$$

$$4MgCO_3\cdot Mg(OH)_2(s) \rightarrow 4MgCO_3(s) + MgO(s) + H_2O(l) \quad (2)$$

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \quad (3)$$

The first two equations represent the weight losses that occur in temperatures ranging 230°C and 380°C, due to evaporation of water hydration molecules and dehydroxilation, respectively. The third equation represents the thermal decomposition of magnesite originated in the process that occurs at temperatures ranging between 340 and 550°C.

Sample SEV3 showed the characteristic peak of the calcitic carbonates decomposition (present in all mortars) along with only the corresponding peak of magnesite decomposition with higher weight losses between 340 and 550°C. Samples SEV2 and SEV4 presented, besides the former compounds, dolomite in its composition.

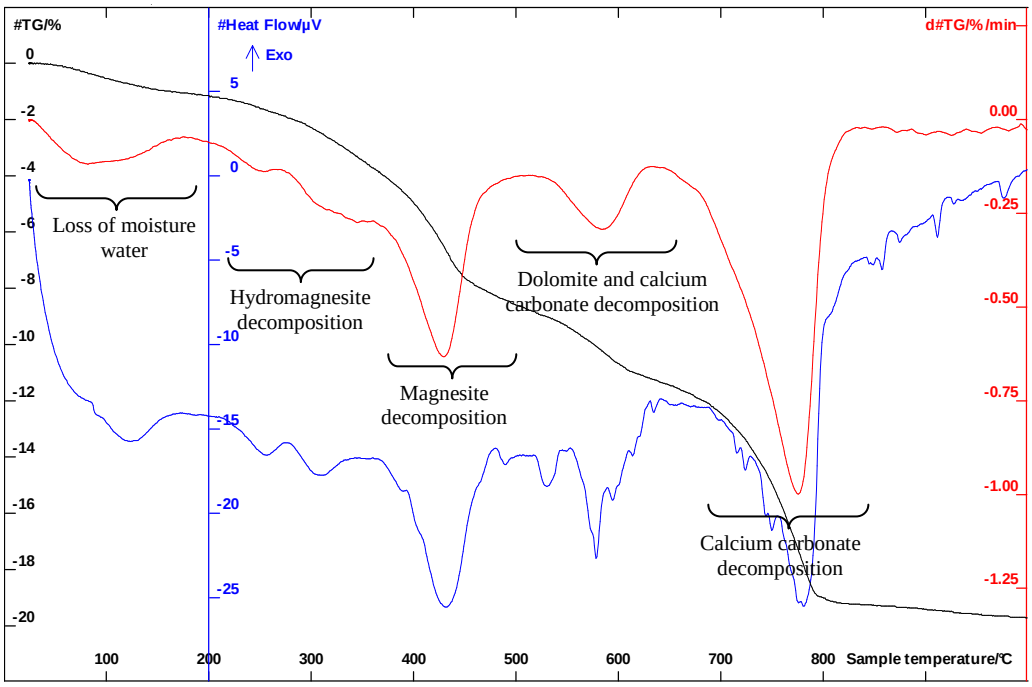

Figure 7: Thermogravimetric curves of sample SEV4.

Tables 3 and 4 show the weight losses corresponding to several temperature ranges, obtained taking into account the mineralogical composition of each sample and the temperature ranges that were defined from the TGA curves.

Table 3: Weight losses (in %) of the samples SEV1, SEV2, SEV3, SEV4 and SEV8.

		Temperature range (°C)				
Samples		**20→200**	**200→340**	**340→550**	**550→900**	**20→1000**
SEV1		1,46	1,98	7,01	12,34	22,93
SEV2		1,78	1,94	7,63	11,27	23,40
	INT	1,55	0,67	7,50	7,79	17,68
SEV3	**IM**	1,46	0,96	7,70	10,15	20,46
	EXT	1,54	0,95	5,77	7,51	15,90
SEV4		1,98	0,90	7,34	7,24	17,89
SEV8	**INT**	1,23	1,21	5,78	5,46	15,81
	EXT	1,76	2,75	9,27	5,74	21,08

Table 4: Weight losses (in %) of the samples SEV6 and SEV7.

	Temperature range (°C)				
Samples	**20→240**	**240→500**	**500→900**	**900→1000**	**20→1000**
SEV6	0,60	1,04	8,54	0,05	10,22
SEV7	0,72	1,28	7,51	0,06	9,58

Chemical and grain size analysis

Table 5 shows the chemical analysis of the soluble fraction which can give valuable information about the composition of the mortars and its environment.

Table 5: Chemical composition of the soluble fraction of the mortars (wt %).

Weight %	SEV1	SEV2	SEV3			SEV4	SEV6	SEV7	SEV8	
			C. INT	C.IM	C.EXT				C.INT	C.EXT
CaO	15,47	15,78	10,41	11,51	10,30	9,14	8,86	8,75	8,46	9,46
MgO	8,34	5,45	6,94	6,98	6,18	7,08	1,39	1,79	5,69	9,64
K_2O	0,05	2,36	0,68	0,88	0,59	0,51	0,34	0,45	0,37	0,35
Na_2O	0,09	3,08	1,87	1,79	0,97	0,90	0,07	0,12	0,46	0,60
Cl^-	0,48	0,85	0,18	0,23	0,16	0,62	0,06	0,06	0,53	0,49
SO_3	0,12	0,12	0,10	0,10	0,10	0,28	0,18	0,15	0,23	0,38

Chloride ion contents obtained in the mortars are one order of magnitude higher than would be expected and even higher than in mortars in high salinity environments (Alessandrini et al, 1991; Sabbioni et al, 2002). Considering that Evora is located far from the sea, thus having an environment with low salinity and that chloride was found in mortars that were located inside the church at different levels, we can assume that salt was added during the manufacture of the mortar with the aim to accelerate the mortars carbonation (hardening).

Samples SEV1, SEV2, SEV3, SEV4 and SEV8 present higher magnesium oxide contents than samples SEV6 and SEV7, which is in agreement with the XRD data which showed that the former are composed of calcium-magnesium carbonates.

The grain size distributions of the insoluble residues are presented in figure 8. As mentioned in other studies (Bakolas, 1998; Maravelaki-Kalaitzaki, 2003; Benedetti, 2004), this analysis is important if one intends to produce compatible mortars for restoration. The grain size distribution revealed that the majority of the samples have aggregates with diameters between 0,315 and 1,25mm. The results also show that the different mortar layers identified within samples SEV3 and SEV8 have aggregates with the same nature and size distribution which is a strong evidence that these layers were prepared at the same period.

For all samples, the insoluble residue observation under stereomicroscope together with the XRD analysis allowed the confirmation that the aggregates used have uniform mineralogical composition which can be correlated with the granitoid rocks from Evora's crystalline massif. It was also possible to verify the presence of ceramic materials.

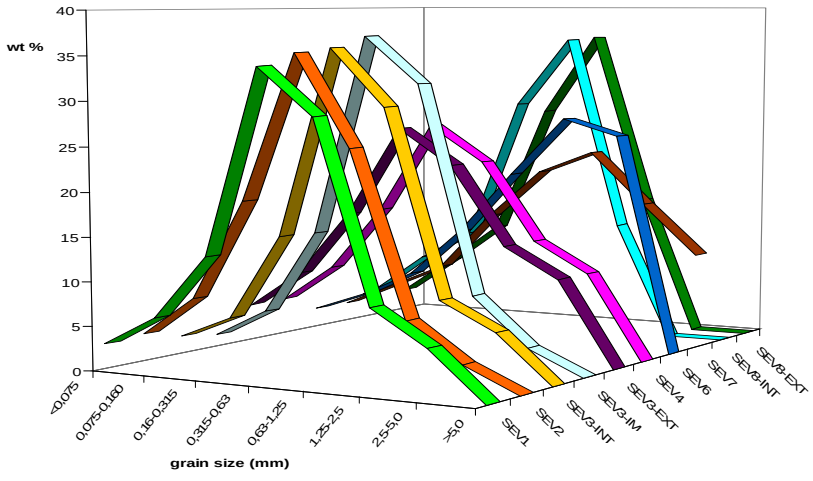

Figure 8: Grain-size distribution of the insoluble residues

Scanning electron microscopy

SEM analysis can give valuable information about the mortars materials namely binder, aggregates and reaction products and allows the observation of their shapes, sizes, textures and distribution in the mortars. Figures 9 to 16 show the most important microstructural features of the studied samples. Analysis of the mortars by SEM/EDS showed that all mortars have a compact gelified microstructure, typical of old lime mortars, with

aggregates well embedded in the matrices. It was possible to identify the nature of the aggregates as mainly lithoclasts of quartz (figure 10a), feldspars (figure 10b) and mica (figure 10c, d).

From SEM/EDS observation of sample SEV1 what stands out is the presence of foliated crystals rich in magnesium, probably hydromagnesite, which were located in porous and superficial areas (figure 12). In this sample, countless biologial colonizations were also observed (figure 11).

Besides the already mentioned features, on sample SEV2 it was possible to observe the presence of halite crystals and aragonite (figures 13 and 14, respectively). The presence of halite, which was also observed in other samples, namely SEV3-INT, SEV4, SEV8-INT and SEV8-EXT, was previously detected by XRD and indirectly by chemical analysis (chlorine ion content).

The analysis done on the three layers that compose the sample SEV3 showed that these mortars are very similar.

In sample SEV4 it was possible to observe very altered micas (figure 10c) and the presence of gypsum (figure15) which was not detected in the mineralogical analysis by XRD.

SEM/EDS confirmed that the samples from the Zimborium Tower, samples SEV6 and SEV7, present a more simplified composition than the others, being composed mainly by calcium carbonate with aggregates composed of granodiorite clasts. In sample SEV7 it was possible to observe $CaCO_3$ crystals in two different forms, calcite and aragonite (figures 9a and 14) and biological colonies in the paste (figure 11).

The most striking observation was the presence of carbon black particles in the mortars (figure 11a) with magnesian binder which can be attributed to combustion of organic materials. The concomitant presence of abnormal amounts of chloride and the presence of these carbon black particles (in mortars from the interior of the church) may indicate that fire was produced inside the church and sodium chloride was added during the making of the mortars to accelerate the mortars hardening. In fact, historical documents indicate that by the XVI century, the rocks from the inner walls of the Cathedral were very degraded so we can assume that this was a technical solution that was envisaged.

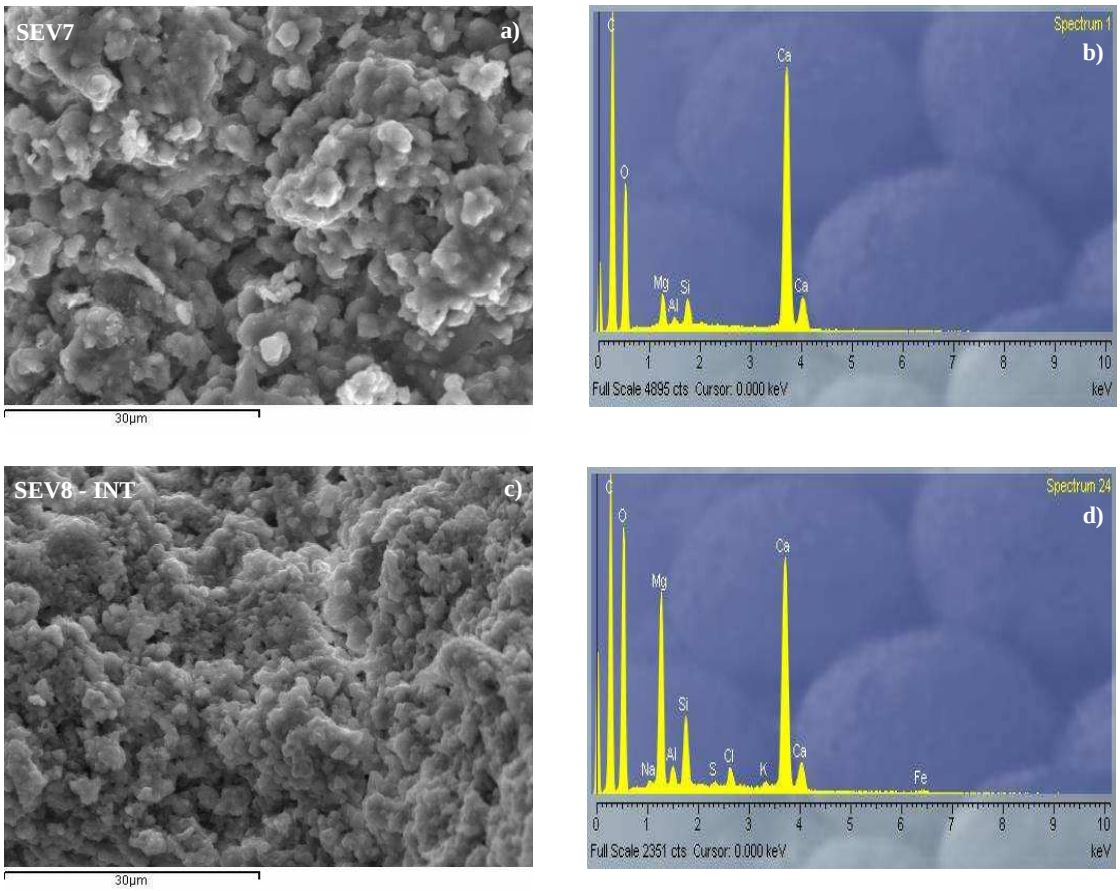

Figure 9: SEM micrographs of the mortars; a) microstucture of the lime matrices of sample SEV7 and (b) corresponding EDS; c) microstructure of lime matrices of the sample SEV8-INT and (d) corresponding EDS.

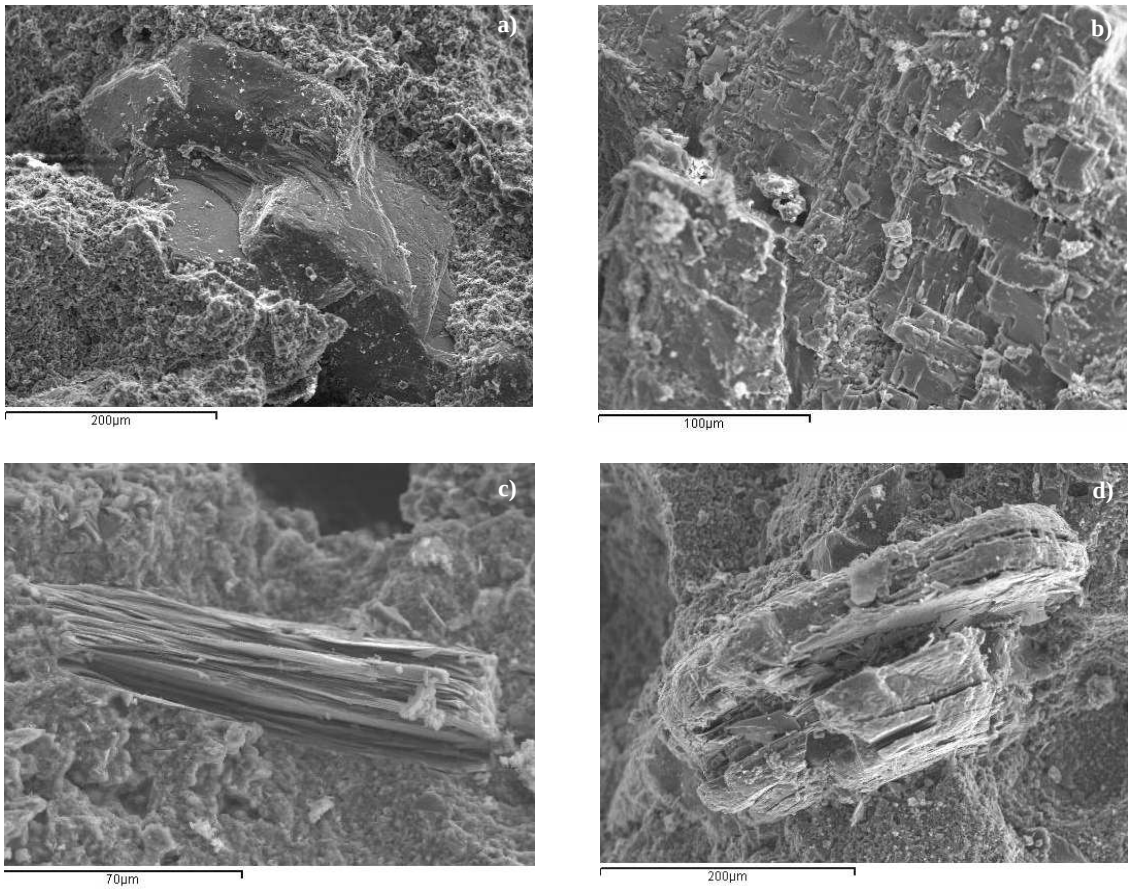

Figure 10: SEM micrographs of the aggregates; a) Quartz grain in sample SEV3-EXT; b) Altered feldspar grain in sample SEV3-EXT; c) Mica (biotite) observed in sample SEV8-INT; d) Mica (muscovite) observed in sample SEV4.

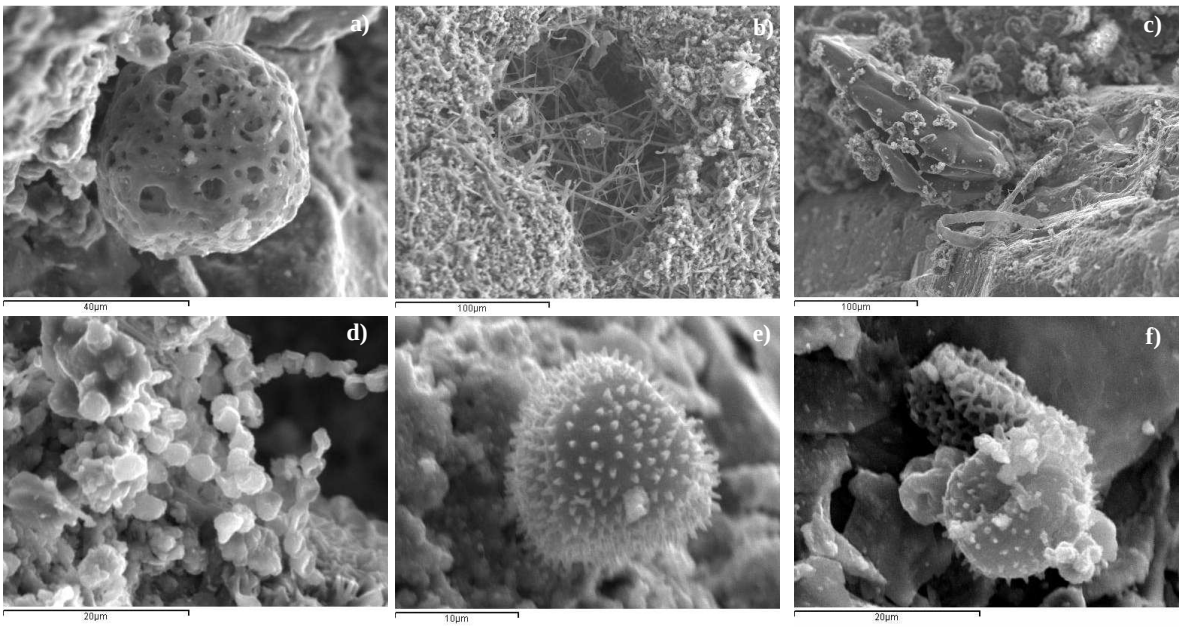

Figure 11: SEM micrographs of a) a carbon black particle typical of combustion emissions (sample SEV4) and different types of biological materials of b) sample SEV1; c) sample SEV2; d) sample SEV2; e) sample SEV2; f) sample SEV4.

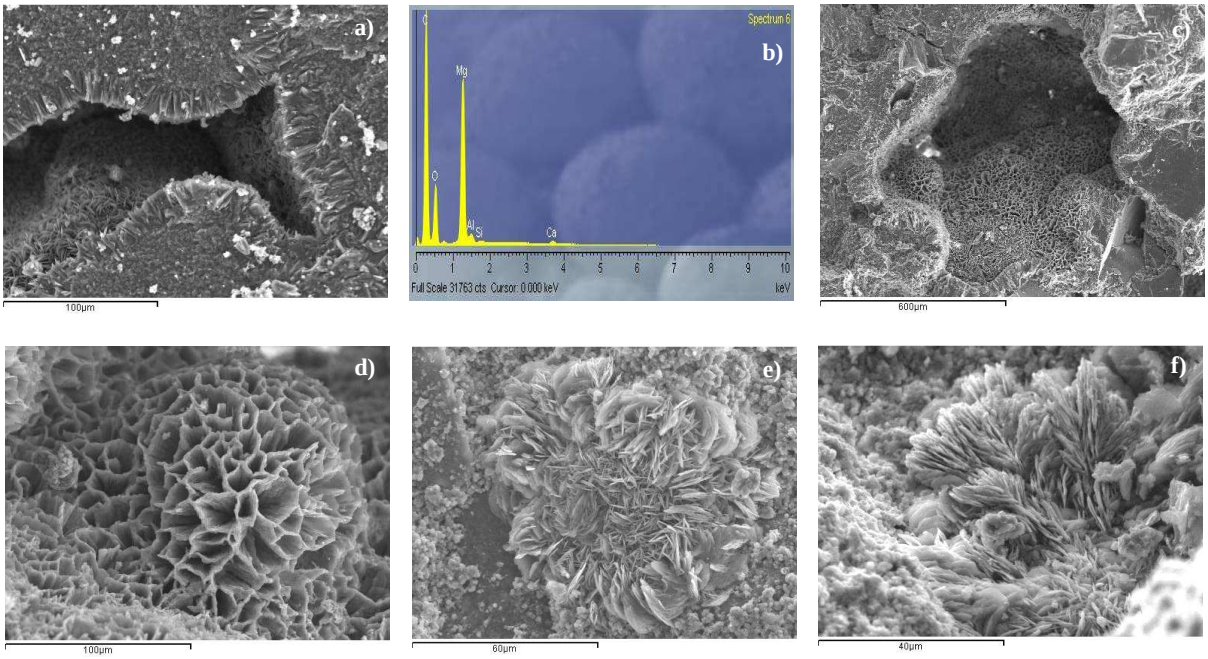

Figure 12: SEM micrographs of hydromagnesite crystals observed on the samples; a) SEV1 and corresponding EDS; c) and d) SEV7; e) and f) SEV3-IM.

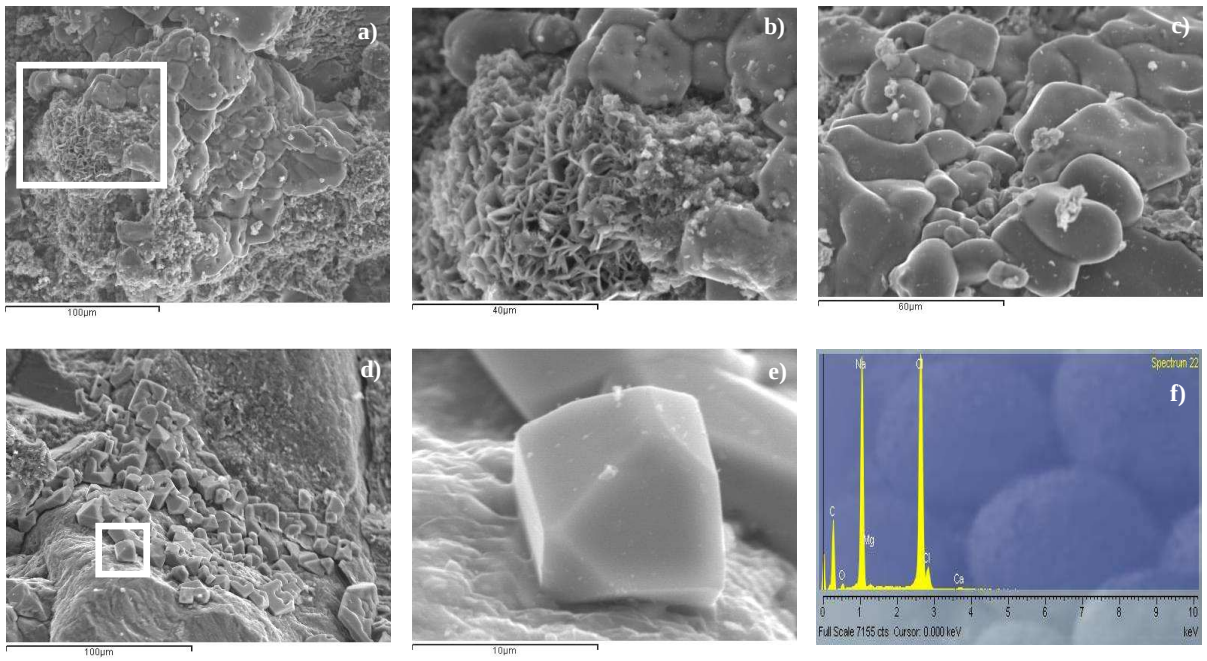

Figure 13: SEM micrographs of halite crystals; a), b) and c) sample SEV2; d) and e) sample SEV8-INT and f) corresponding EDS spectrum.

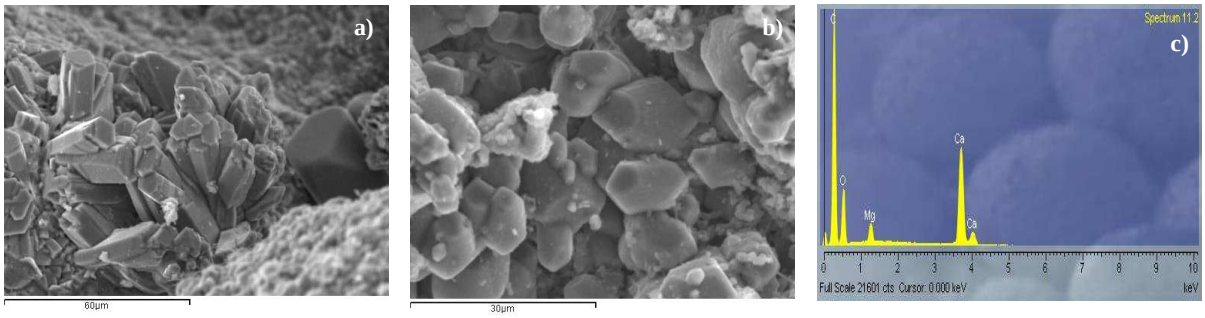

Figura 14: SEM micrographs of aragonite crystals: a) sample SEV2; b) sample SEV7 and c) corresponding EDS spectrum.

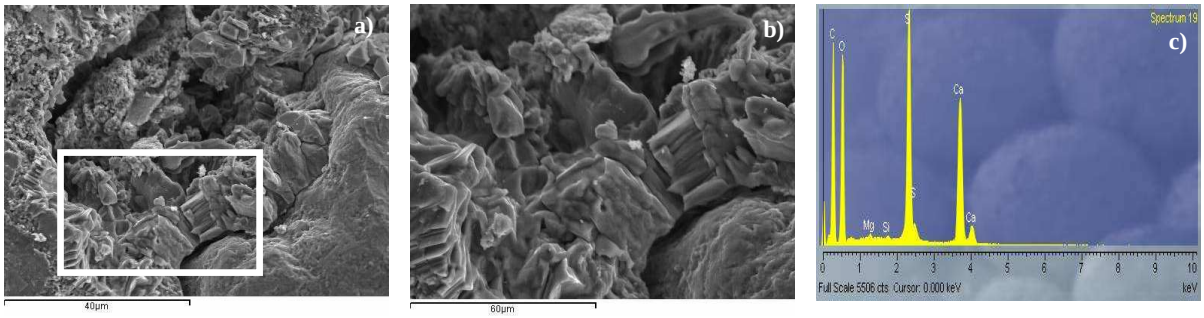

Figura 15: a,b) SEM micrographs of gypsum of sample SEV8-INT and c) corresponding EDS spectrum

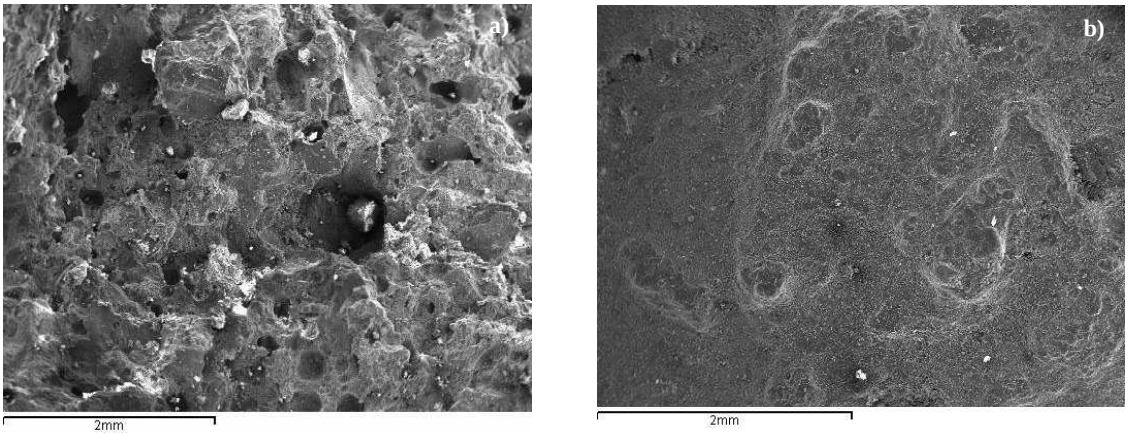

Figura 16: SEM micrographs; a) sample SEV8-INT; b) sample SEV8-EXT.

Mortar composition

The simplified compositions of mortars are fundamental parameters for the preparation of compatible mortars and can be used together with the results from other techniques, to evaluate mortar behavior and correlate with their chemical, mineralogical and mechanical properties. These simplified compositions (table 6) were calculated on the basis of the method designated as ”Jedrzejewska” (Jedrzejewska, 1960) referring to old lime mortars combining the calcium carbonate % estimated by TGA/DTA with the residue analysis. As mentioned before, all mortars, with exception to samples SEV6 and SEV7, showed the presence of magnesium compounds, which indicates the use of dolomitic lime, and therefore the composition of each phase was calculated from the correspondent weight losses.

Table 6: Simplified composition of the mortars (%).

Samples		Aggregate[(1)]	Calcite[(2)]	Magnesite[(3)]	Dolomite[(4)]	Hydromagnesite[(5)]	Soluble fraction[(6)]
SEV1		52	28	6	-	13	1
SEV2		60	26	11	-	-	3
SEV3	**INT**	63	18	14	-	-	5
	IM	59	23	15	-	-	3
	EXT	66	17	11	-	-	6
SEV4		63	13	10	7	2	5
SEV6		78	19	-	-	-	3
SEV7		78	17	-	-	-	5
SEV8	**INT**	66	12	8	7	1	6
	EXT	59	13	7	5	12	4

(1) Aggregate = insoluble residue of contents
(2) Calcite = $CaCO_3$ content determined by TGA
(3) Magnesite = $MgCO_3$ content determined by TGA
(4) Dolomite= $CaMg(CO_3)_2$ content determined by TGA
(5) Hydromagnesite = hydromagnesite content determined by TGA and chemical analysis
(6) Insoluble fraction = 100 – Σ (Aggregate + Calcite + Magnesite + Dolomite + Hydromagnesite)

Conclusions

Our work on the characterization of Evora's Cathedral mortars has shown the use of two types of binders, dolomitic and calcitic. Samples SEV6 and SEV7, both from the Zimborium Tower, are calcitic aerial lime mortars and have similar compositions which are in agreement with previous historical research that pointed out the probable date in the 14th century.

On the other hand, mortars from inside Evora's Cathedral, (SEV2, SEV3 and SEV8) proved to be dolomitic aerial lime mortars with similar compositions in regard to type and proportion of aggregates. These results contradict previous information that pointed out different ages for each mortar. Instead, this work shows that these mortars were most certainly produced at the same period, probably in the 16th century, which is the century when the high choir wooden chair structure was built.

Samples SEV3 and SEV8 are composed by several layers applied at the same period, as indicated by their similar components. Probably, these renders are multilayer systems, including regularization and finishing coats, commonly used on ancient masonry to improve protection and esthetic appearance of the wall.

The aggregates used in all mortars have a mineralogical composition identical to the granodiorites of Evora region. Moreover, the grain morphology indicates that the aggregates used in the manufacture of the mortars were produced from crushed rocks, probably from the rocks used in the walls construction, and the identification of olivine indicates that the most probable provenance source of these aggregates was the *Alto de S. Bento* quarry.

The systematic presence of high amounts of chlorine and the presence of carbon black particles in the dolomitic mortars may indicate that smoke was produced and salt was added to accelerate the carbonation process and hence the mortars hardening.

This work demonstrated the need to use a methodology which combines different physical, chemical and mineralogical characterization techniques for the study of old mortars enabling a deep insight on the mortars composition, historical and technical background and state of conservation.

Optical and electron microscopy proved to be indispensable techniques for the characterization of these materials. Without these techniques it wasn't possible to detect neoformation/alteration compounds and biological materials that, in most cases, are only present in very small quantities and, therefore, very difficult to detect with other techniques.

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