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CHARACTERIZATION OF MATERIALS USED IN THE QUART TOWERS (VALENCIA, SPAIN) PRIOR TO RESTORATION

M. Ramírez[1], J. Llinares[1]*, M. Soriano1, B. Sáiz[2], J. Curiel[3]

[1]Departamento de Construcciones Arquitectónicas.
[2]Departamento de Expresión Gráfica Arquitectónica.
[3]Departamento de Física Aplicada.
Universidad Politécnica de Valencia, Camino de Vera S/N. 46022. Valencia

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Corresponding author: Jaime Llinares Millán (jllinares@csa.upv.es)

ABSTRACT

Quart Towers are one of the remaining gates in the medieval wall of the city of Valencia (Spain). They were built in the 15th century and have recently been cleaned and consolidated. Prior to this work, a multidisciplinary team conducted a physicochemical study to diagnose the state and composition of different materials. Stone, mortar, patinas, salts etc., have been analyzed as well as their state of deterioration Remains of previous interventions have been found in mortars of restitution and application of consolidants that have caused damaging salts. The methodology used is optical microscopy, X-ray diffraction and scanning electron microscopy with X-ray microanalysis. The results have been used together with documentary data to identify the components of the materials in order to, if possible, compatibility the material in the damaged areas and to determine the most appropriate techniques and procedures for applying cleaning systems, enabling consolidation and protection of the building without altering the unique characteristics of the original building typology.

KEYWORDS: Characterization materials, historical buildings, lime mortar, old mortars

1. INTRODUCTION: THE QUART TOWERS

The city of Valencia (Spain) is on the Mediterranean coast and since ancient times has been an important city of commerce. The ancient city is of Roman origin and with concentric growth its appearance has been preserved. Figure 1 shows the outlines of the different walls (Roman, Islamic and Christian) throughout history. New development in the 19th Century, far from erasing the remains of the medieval city consolidated its structure, and remaining in the middle of contemporary urban development (Da Fonseca et al, 2007)

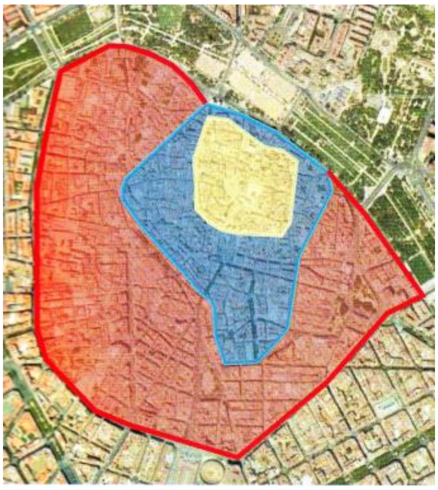

Figure 1 Roman wall in yellow, Islamic wall in blue and Christian wall in red.

The Christian wall was built in the mid-14th Century. It had a perimeter of over 5,000 m but very few remains are still visible. 12 gateways were built in this wall, one of which was the Quart gateway and and in the 16th and 17th Centuries the number increased to 15. The type of construction for these access points was the tower-gateway.

The Quart Towers were built in the 15th Century, when Francesc Baldomar started construction in 1441. Construction of the new Quart gateway had to take into account the problem of the angle of the street to the outline of the wall. Francesc Baldomar resolved the problem by building the gateway and the towers with a deviation that did not alter either the path or the wall (Fig. 2). In 1460 Jaime Pérez took over the works followed by Pere Compte who worked on the towers up to the end of 1468. In 1474, Pere Bonfill continued the work and finished the towers in 1493. Despite being mainly a defensive work, their monumentality and beauty meant they were perfectly integrated in the city.

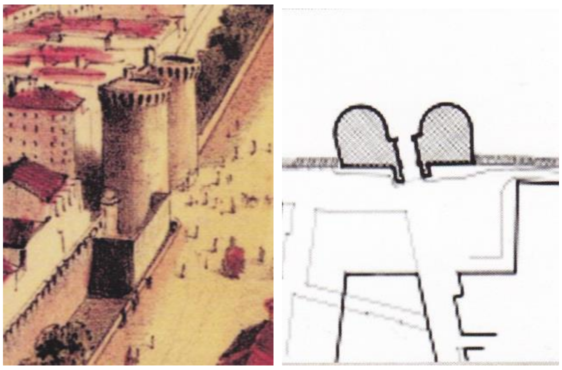

Figure 2 Layout of the Towers in relation to the wall.

These two 34 m high towers are cylindrical on the outside and flat on the inside and are a clear example of late Gothic military architecture. They are joined by a rectangular construction with a door with a semicircular arch surrounded by ashlar work/masonry, which housed the guardian angel and now houses the city's coat of arms. The Quart towers were built with masonry and have very little decoration. They were mainly built using natural stone from the quarries near the city of Valencia and an agglutinative, air lime. The mixture of lime with earth and natural arids with different granulometry obtained very consistent products (mud wall, mortars) for building the towers' deep high walls. These materials were also used on the walls in the wide interior space of the building with vaults of brick arches or natural stone groin vault (Fig. 3). Air lime was also widely used to protect natural stone elements from the weather (battlements, keystones, etc.) with a film or layer of carbonated lime. Except in areas very exposed to the wind or running water even today, mainly south-facing tower, a layer of reddish-orange colour due to the addition of natural earth can be seen on this exterior layer.

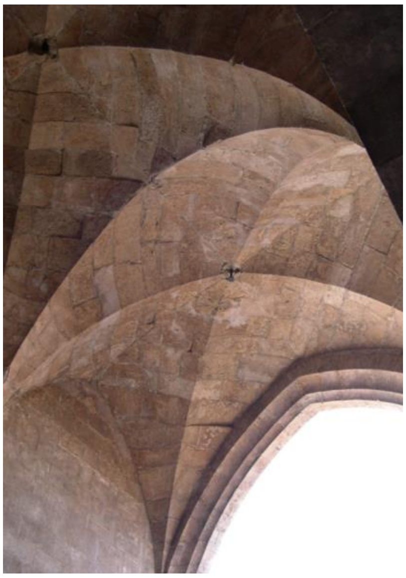

Figure 3 Groin vaults.

The building has been used for centuries for different purposes, ranging from a women's prison to military one. Since it was built this huge building has witnessed the city's important historical events. The outside of the monument continues to show signs of the bombing suffered when the French lay siege to the city in 1808 (Bercher Gómez. 1983; Garín Ortiz de Taranco, 1978; Gómez Bayarri, 2009). Time and the different uses have aged the towers which show deterioration in the materials and alteration in some of the construction elements.

Before dealing with the restoration of monuments of historical interest as in this case, information is needed on the materials used and their state of alteration. Furthermore, any cleaning operation requires a prior stratigraphic study of the surface to be cleaned with the aim of identifying remains of patinas, renders or polychromes (Moropoulou et al, 1995). Various techniques can be used such as optical microscopy, scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), differential thermal analysis, etc. (Soriano, 1996; Riccardi et al, 1998; Alvarez et al, 2000, Moropoulou et al, 2000, Gleize et al, 2000; Sánchez-Moral et al, 2000, Genestar and Pons, 2003; Bianchini et al, 2004; Elsen et al, 2004; Elsen, 2006; Velosa et al, 2007; Adriano et al, 2009; Marrocchino el al, 2010; Sanjurjo-Sánchez, 2010; Mirielo et al, 2011; Drdácký et al, 2013; Yaseen et al, 2013).The aim of this study is to characterize the materials in the different construction elements, especially the materials that show alteration or deterioration, in order to establish the origin, causes and process of the alterations. This study has served to indicate the treatments for cleaning, replacing and consolidating the materials in the recent restoration (Fig. 4).

Figure 4 Quart Towers after restoration.

2. EXPERIMENTAL

After a preliminary visual inspection of the state of the monument and analysis of the existing documentation, sampling was carried out before and during the intervention from the interior and exterior of the towers, the battlemented walkway between them, the vaults, arches, etc., including samples of stone, rendering mortars from both towers, cladding mortars from interior spaces, filling mortars for joints between the blocks of stone or the bricks in the vaults, dirt deposits of different thickness on the renderings and natural stone, patinas, salt deposits and even remains of ammunition. The preliminary step to analysing the samples was to observe them through optical microscopy (Nikon

SMZ10A) to determine the most appropriate technique for analysis.

The samples were observed at higher magnification and their composition determined with a scanning electron microscope Jeol 6300 with EDX and Oxford Link Isis and Inca software. For the stratigraphic study, the samples were put in resin and vaporised with carbon and in some cases, gold. Crystalline compounds were determined using a Philips X-ray diffractometer with a PW1830 generator and proportional counter, operating at 20 kV and 40 mA, Ni-filtered Cu Ka radiation, in the range 5-80° 2q using a step interval of 0.02° 2q. The software X'Pert HighScore Plus 2.1 was used to identify the mineral phases.

3. RESULTS

Alteration of the materials was evaluated (Fig. 5, 6, 7, 8) and found to be attributable to different causes:

a) *physical and/or mechanical:* the action of environmental agents (water, wind, soot, dust, etc.), the use of the towers, previous interventions (inappropriate treatments in some cases), military actions which caused canon ball damage during the Napoleonic campaign (1808-1809).

b) *chemical:* chemical transformations with decomposition, disintegration, dissolution or decolouration of the materials, reactions caused in the materials due to environmental actions such as, for example, traffic near the towers or the treatment products applied in previous interventions.

c) *biological:* biodeterioration due to bird droppings, plant growth, lichen development, etc. The continuous cladding on the exterior layer of the towers has been characterised (Fig. 9) and the restitution layer applied to some areas in a previous intervention.

Figure 6 Fragments of rendering on the north tower with loss of adherence.

Figure 7 Attack from bird droppings.

Figure 8 Growth of lichens and moss.

Figure 9 Details of an area of the North tower.

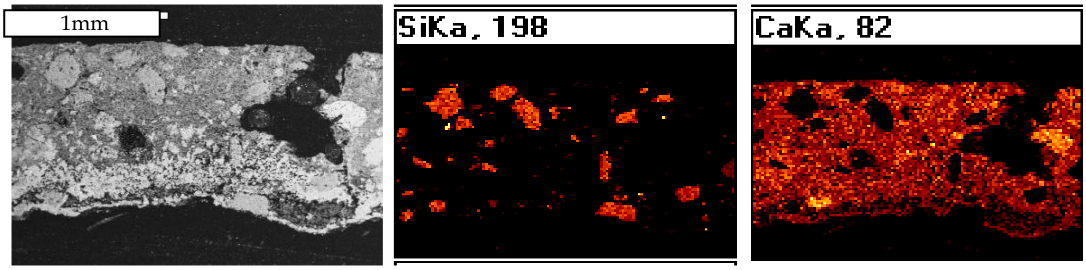

Figure 10 Original exterior rendering on the towers. Microphotography at 50X. Mapping of Si and Ca.

The results confirm that the original cladding for the towers was lime mortar with silica aggregate (Fig. 10). The exterior restitution mortar is also a lime mortar with two types of air lime, dolomitic and calcitic. EDX microanalysis also confirms the presence of S, Al, Cl, Na, Mg and K. XRD in this mortar coloured with natural earth pigments with aluminium silicates and iron oxides (Fig. 11). Cl and Na are also present in other areas corresponding to sea spray as Valencia is on the Mediterranean coast.

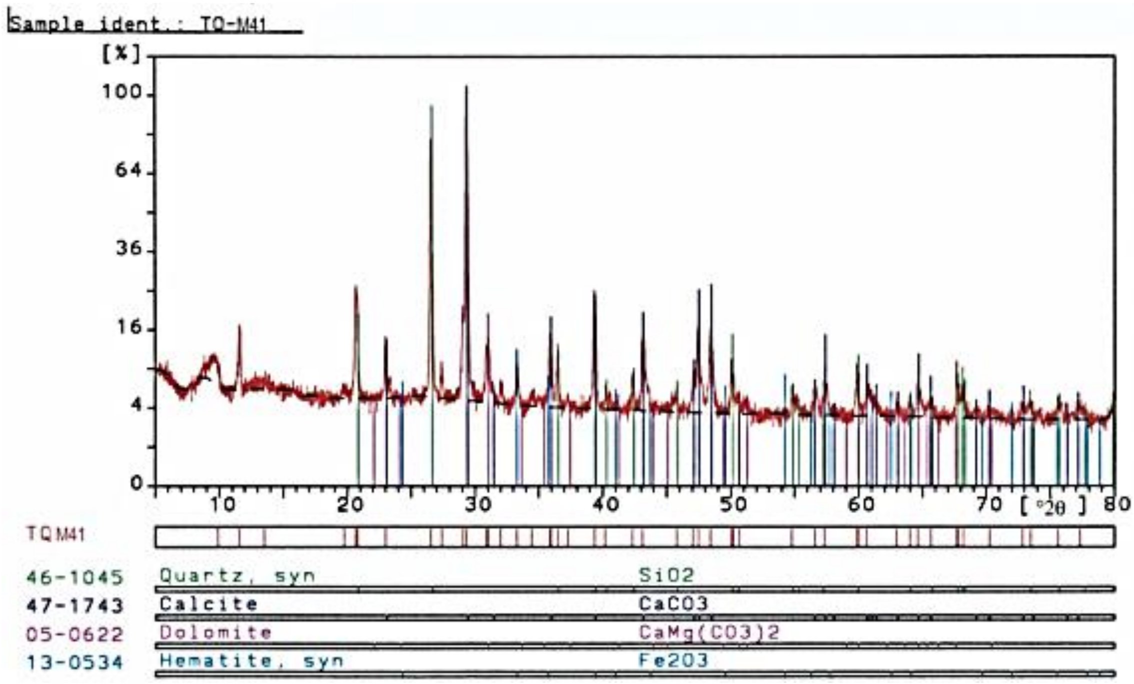

Figure 11 XRD of the restitution mortar.

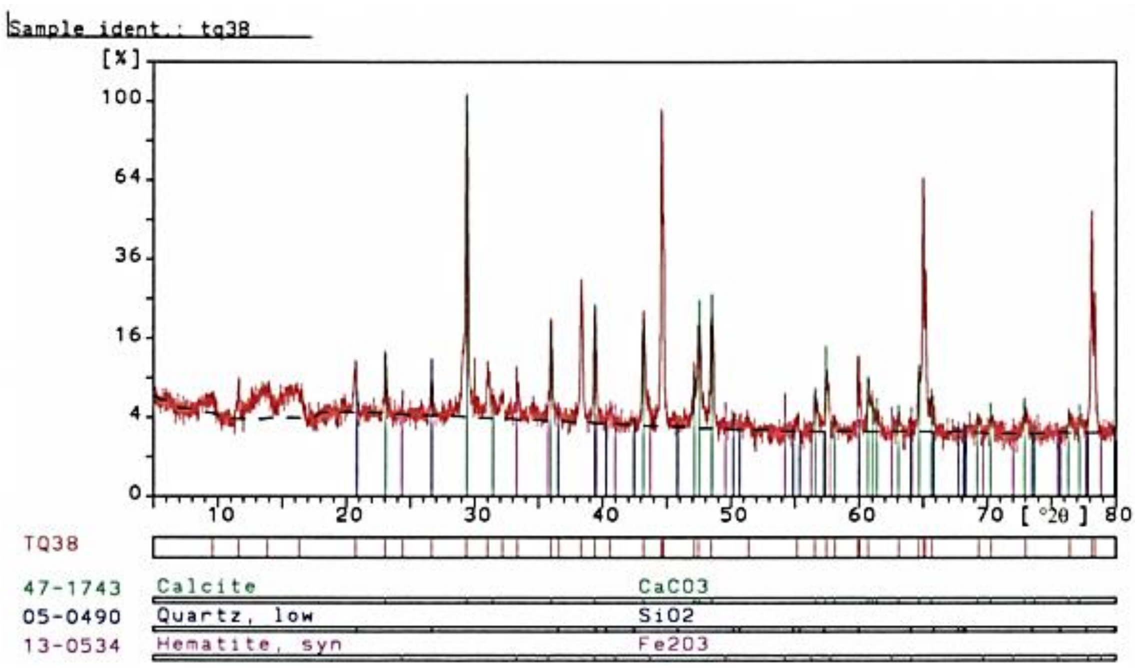

Figure 12 XRD mortar next to stone.

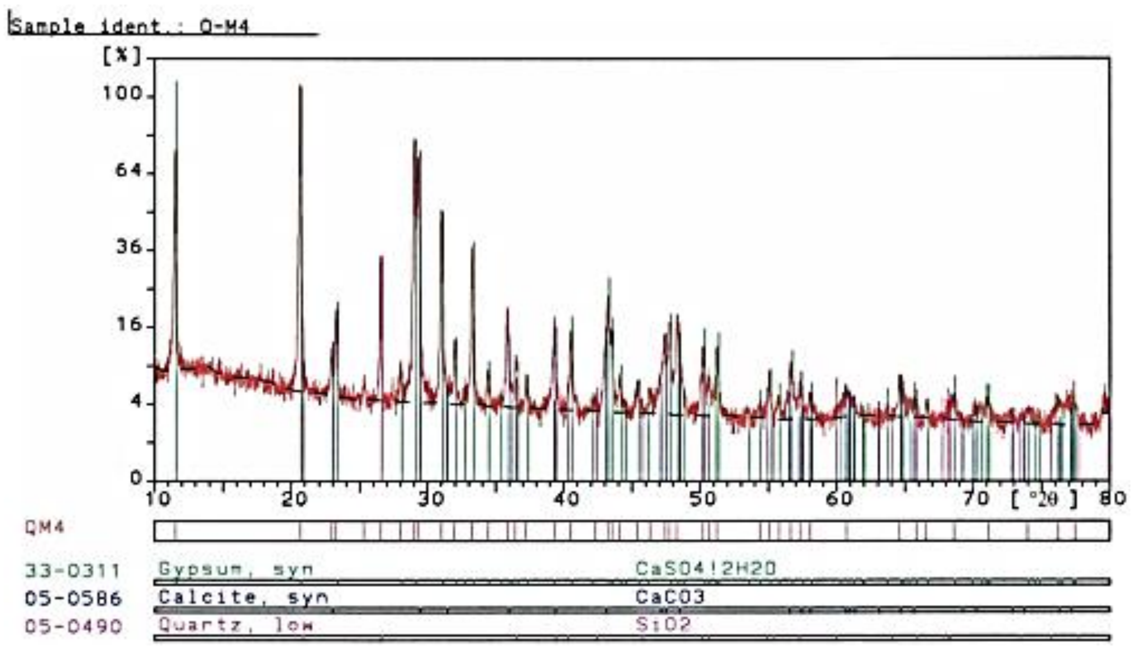

Figure 13 XRD cladding mortar.

The stone is limestone and analysis of the mortar used in the joints of the stone and the central battlemented passage (Fig. 14) shows a lime mortar with silica arid coloured on the surface with natural earth pigments (Fig. 12). The patina on the stone also has the same composition.

There is also an interior cladding, and Fig. 15 shows a back view of the towers with the interior vaulted spaces.

The cladding is plaster with lime paint on the outside. Fig. 16 shows the elemental analysis and XRD sample of the compounds present (Fig. 13).

Figure 14 Detail of the battlemented passage.

Figure 15 Back view of the towers.

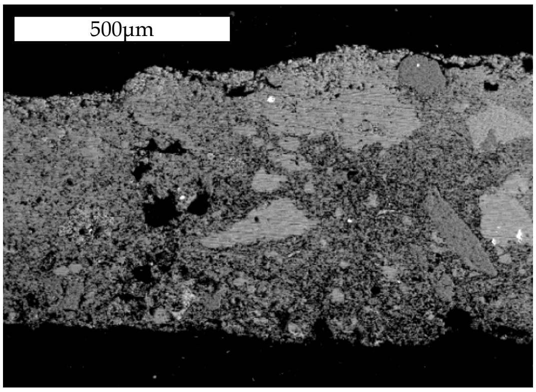

Figure 16 Microphotography of the sample at 100X and EDX analysis.

The mortar on the wall of the staircase in the south tower has been analysed and is a lime mortar with calcite and dolomite.

In the deposit of dirt on different materials, (stone, mortars, etc) plaster neoformation deposits have been observed. The black colouration is due to the presence of carbonaceous products of pollution like soot, dust among others. The results are presented for the masonry work on the battlemented passage in microphotographs at different magnifications and mapping of the distribution of elements in the sample (Fig. 17 and Fig. 18.).

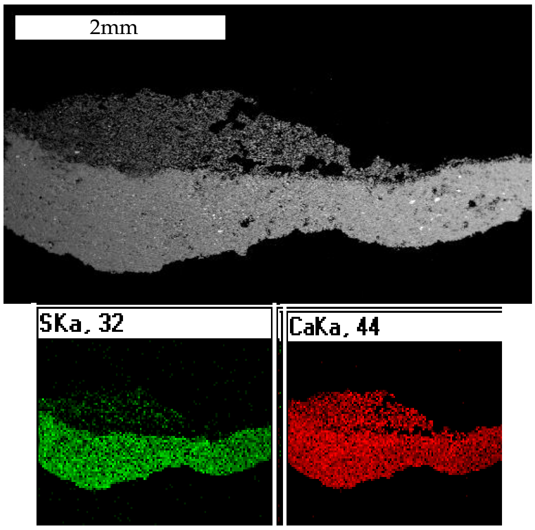

Figure 17 Microphotograph at 25X and mapping of S and Ca.

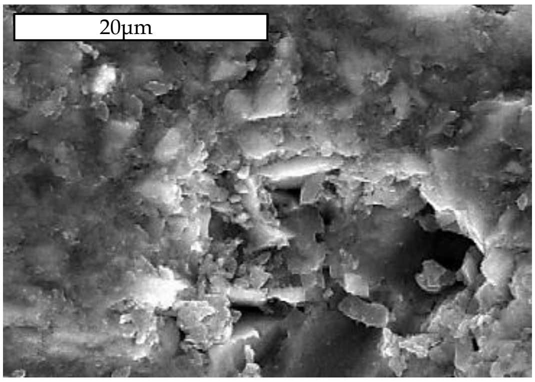

Figure 18 Microphotograph obtained at 3000X.

Figure 19 Detail of the vault in the central block.

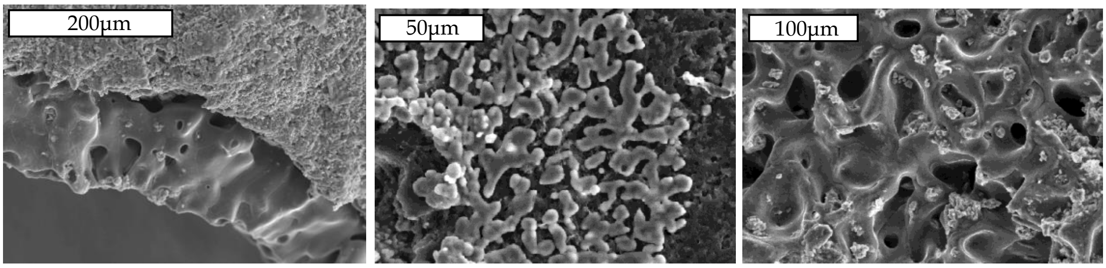

Figure 20 Exterior layer with potassium. The images shows the precipitaded silica gel

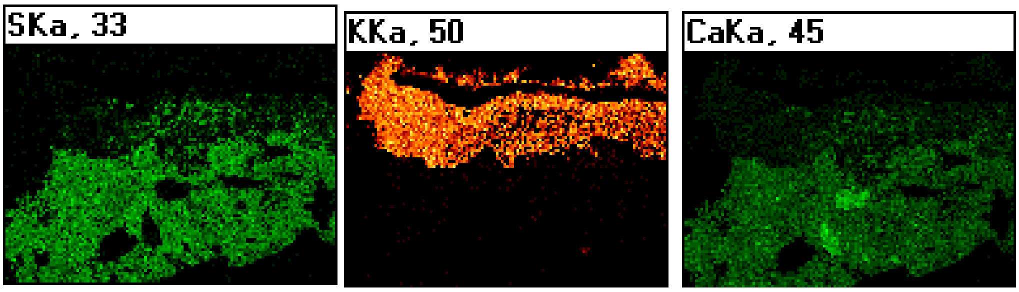

Figure 21 Transversal section. Mapping of S, K and Ca of the silica gel.

Observation of the vault exterior in the interior space of the central block shows the dark polychromy of the false ceiling. (Fig. 19) and X-ray microanalysis indicates that a pigment called mineral black was used, whose composition is based on iron and manganese oxides.

Figure 19 shows a potassium compound created by the application of a consolidant in a previous intervention. The analytical results suggest that the product used was potassium silicate. That consolidant is usually applied by dissolution in acidulated water, generally with hydrochloric acid and this has given rise to the precipitation of a transparent vitreous silica gel (Fig. 20) together with other reaction products such as KOH. The mapping of the transversal section shown enables evaluation of the distribution of the elements (Fig. 21) with plaster mortar beneath the aforementioned consolidant. In some areas the KOH compound has reacted with SO_3 giving rise to potassium sulphates which are damaging salts for the stone (Fig. 22).

The products used in the restoration for cleaning, consolidation and protection have been the subject of analytical control.

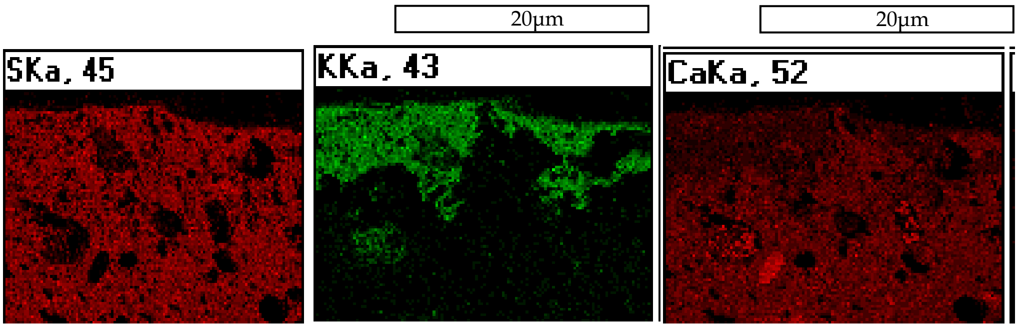

Figure 22 Transversal section. Mapping of S, K and Ca.

4. DISCUSSION & CONCLUSION

The following conclusions can be drawn from the results of the analysis of samples of different construction materials in the Quart Towers.

The stone is limestone with a reddish patina over some of the stone surfaces. The stone has black deposits which are calcium sulphate crusts (newly formed plaster) and the average thickness of the layer is 1 mm, caused by reaction of the stone substrate with pollutants present in the atmosphere (heavy urban traffic in the surrounding area). The black colour is due to the presence of carbonaceous products of pollution like soot and dust. The filler material for the joints between stones is calcium mortar with a reddish colour on the surface and the pigments found are natural earths. Part of the salts, affecting the external sides of the building, correspond to sea spray.

The exterior rendering of both tower blocks is lime mortar with a reddish layer (caused by the addition of natural earths with iron oxides) and neoformation plaster on the surface. In some areas where the material has been replaced the presence of dolomite indicates that dolomitic materials were used to produce the air lime for these mortars, and so two types of binders were used, dolomitic and calcitic limes.

Renderings on the interior surfaces are mortars whose composition varies depending on the room and area. Plaster mortars and lime mortars have been found and on some faces the renderings are formed by a layer of lime mortar followed by plaster mortar finishing on the outside with a fine layer of lime paint. On the vault in the central block remains of the application of a previous consolidant have been found. The product used is currently not recommended because it has been shown to generate new salts and form harmful films.

The in situ study of the construction materials, their state and the modifications they have undergone and the analytical results permit certain recommendations on the appropriate cleaning, consolidation and protection treatments. Limestone in general has acceptable compactness and therefore plaster crust neoformation can be eliminated without damaging the stone by a controlled solid microprojection system that will respect the natural and artificial patinas present on the stone. This waterless system also enables the removal of biodeterioration process symptoms (bird droppings, moss, lichens, etc..) and saline deposits.

Depending on the area, the renderings present an uneven state of alteration and a variable composition. Replacement renderings have been found on the inside and outside of the towers. Hence a particular specific treatment is recommended for temporary pre-consolidated areas where efficient cleaning is required that does not cause damage and dissolvent cleaning systems are always avoided as they encourage further separation between rendering layers as well as fissuring, cracking and disintegration. In some areas, detachment is imminent without the need to act on it and so the cladding will necessarily have to continuously restored to a state that faithfully respects the texture and composition of the original materials used during construction of the building.

The cleaning, consolidation and recovery works have enabled the Quart Towers to show their great structural beauty.

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