Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 40 (2013) 525 – 529
Energy Procedia

European Geosciences Union General Assembly 2013, EGU

Division Energy, Resources & the Environment, ERE

# Characterization of Compounds Formed and Added on Surface of Outdoor Seville City Hall

M.D. Robador[1], F. Arroyo[2,] J.L. Perez-Rodriguez[3,*]

[1] *Technical Architecture Faculty University of Seville, Avda. Reina Mercedes s/n, 41012 Seville, Spain.*

[2] *Departamento de Ingeniería Química y Ambiental. University of Seville.*

[3]*Materials Science Institute of Seville (CSIC-Sevilla University), Americo Vespucio 49, 41092 Seville, Spain.*

**Abstract**

The study of the stone surface was helpful before the restoration of the Sevilla City Hall façade. This study supplied information of the environmental factors affecting the stone and the restoration treatments used in previous interventions. The stone was thin grained carbonate constituted essentially by fragments of bioclasts and fine sand. The stone was covered by an acrylic resin. Black crust was found. Gypsum and mortars has been added to cover losses of pieces or to fix fragments of stones. A layer of lime on the surface was also detected.



*Keywords*: cultural heritage;stone;mortar;gysum;lime

## 1. Introduction

For centuries the stone façade of Seville City Hall has suffered different restoration interventions. The conservation treatments and the effects of the environmental pollution are both responsible for formation and deposition of different chemical compounds on the surface of the monuments.

The building of the City Hall of Seville is one of the more important samples of the plateresque architecture in Andalusia. The construction of the building started at 1526 by Diego de Riaño who was in

* Corresponding author. Tel.: +34-954-489532; fax: +0-000-000-0000 .
*E-mail address:* jlperez@icmse.csic.es.


doi:10.1016/j.egypro.2013.08.060

charge to make a stone building with façade to the Major Plaza of the city. After his death the work was performed by Juan Sanchez.

The façade stone has been study previously and a good knowledge of its mineralogy and structure is actually well known. Guerrero Montes [1] realized the diagnosis of the current condition of conservation of the monumental façades of the City Hall of Seville. This author identified the litotypes of stones used in the construction of the building and the alteration of these materials. Other studies about this stone have been carried out by Barrios Padura et al [2] and Duran et al [3].

To realize so exceptional plateresque façade of Seville City Hall a soft stone was selected to carve easily the stone. The carved stone presents a high surface of attack for the external agents. For centuries the facade has been restored several times with more or less success.

Before the restoration of the City Hall façade, the study of the stone surface was very helpful. This study supplied information of the environmental factors affecting the stone and the restoration treatments used in previous interventions.

## 2. Experimental

### *2.1. Materials*

The façade of the Seville City Hall is showing in figure 1.

Fig.1. Façade of the Seville City Hall

### *2.2. Methods*

The following methods have been used: X-ray diffraction (XRD), thermal analysis (differential thermal analysis (DTA) and thermogravimetric analysis (TG)), petrography microscope, non-destructive portable X-Ray fluorescence (XRF), scanning electron microscope (SEM), energy dispersive X-Ray (EDX) and infrared transformed Fourier (IRTF).

## 3. Results

The petrography study of the stone used in the construction of the plateresque façade confirms the presence of a carbonate stone of thin grain constituted essentially by fragments of bioclasts and fine sand.

The study by scanning electron microscopy of small fragments showed a compact and continuous cover that suggests a polymer layer (fig. 2). The IRTF spectra obtained in the external surface (fig. 3) showed absorptions bands at 2849, 2873, 2957, 2980, 1732, 1448 and 1324 $cm^{-1}$ attributed to acrylic resin. The band at 1116 $cm^{-1}$ was attributed to gypsum. The mass spectroscopy of the black crust showed the presence of alkanes produced by petrol combustion. Other organic compounds were also detected as isoprenic hydrocarbons, fatty acids, amides and polycyclic aromatic hydrocarbons. These organic compounds have been found also in other monuments of Seville [4, 5]. The XRD analysis of the black crust showed the presence of gypsum with calcite and quartz. The chemical analysis carried out by EDX in the SEM showed also the presence of microspherules of different chemical composition.

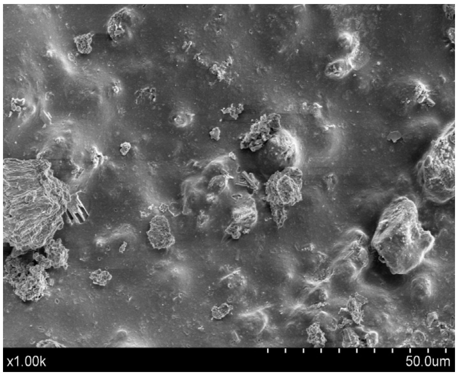


Fig.2. Microphotography by SEM

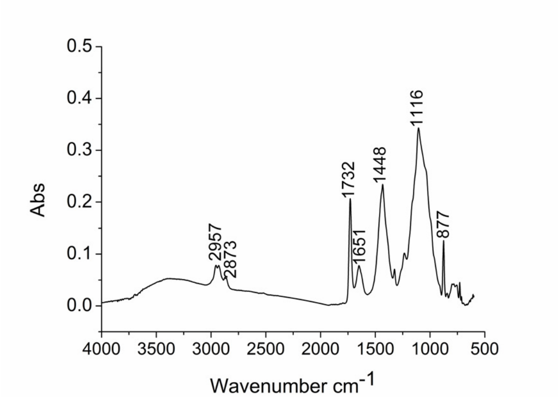


Fig.3 FTIR

The mineralogical composition was calculated using the XRD (fig. 4) and the thermal study (figs 5 and 6). The phases present was determined by XRD. Calcite and gypsum percentages were determined in the thermogravimetric curve using the mass loss between 650 and 800ºC and 100 and 200ºC, respectively. The organic matter % was determined by the mass loss between 200 and 600ºC that showed an exothermic effect with two maximums in the differential thermal curves. Figure 5 showed the DTA and TG curves of the stone.

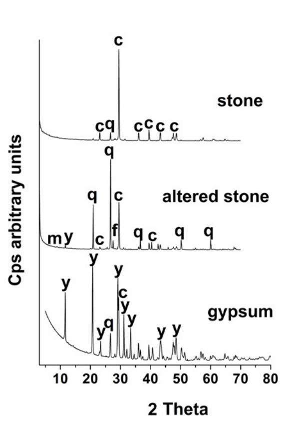


Fig. 4. XRD of studied materials: c:calcite, q: quartz, y: gypsum, m: mica, f: feldspars

Table 1. Mineralogical percentage of studied materials

| Sample | stone | Altered stone | gypsum | mortar |
|---|---|---|---|---|
| Calcite | 95 | 60 | 5 | 40 |
| Quartz | 5 | 40 | | 50 |
| Gypsum | 2 | <5 | 95 | 5 |
| Organic matter | | | | 1 |
| Mica | | <5 | | >5 |
| Feldspars | | <5 | | <5 |

The XRD of stone showed the presence of calcite and quartz (fig 4). The concentration of calcite in the stone was calculated about 95% (Table 1) and quartz percentage about 5 %. In all samples was also detected the presence of small percentages of gypsum (between 2 and 5%).

Reposition materials were observed covering losses of pieces and fixing fragments of stones. Gypsum is the main component of these samples (80-95%) according with the XRD (fig. 4) ant TG studies (fig 6). Other materials used, similarly that the gypsum previously describes or used to join stones pieces were characterized as mortars. These materials were constituted by calcite and inert material, mainly quartz. In addition, feldspars and mica appeared. One of these samples is a material constituted by calcite 40%, quartz 50%, mica < 5% and feldspars <5%. Disaggregated stone showed a high concentration of gypsum (45%), quartz (15%) and calcite (38%) in the external area. In internal parts of the sample the calcite percentage increased to 60%. These data suggested that this sample has been altered by the effect of the environmental contamination, mainly by $SO_3$. The calcite content decreased in comparison with the original stone (no-altered) being the alteration higher in the external part of the sample. Gypsum was also found in the interior of the stone confirming that it has emigrated due the high porosity of the stone.

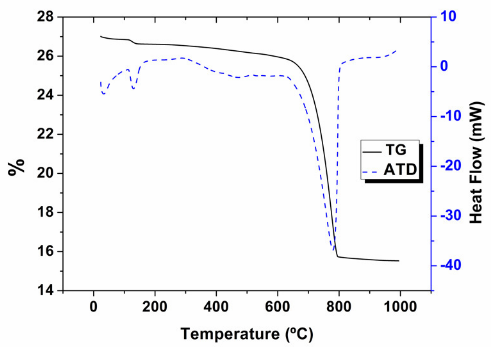


Fig.5. ATD and TG curves of stone

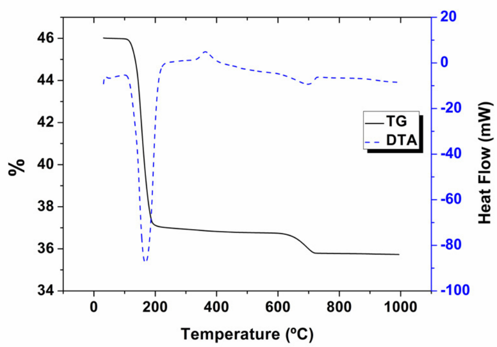


Fig. 6 ATD and TG curves of superficial material

In previous interventions of this façade, not suitable materials, as gypsum, cements mortars, acrylic polyester, etc were used.

In some areas of the façade possible wall paintings were detected. A cross-section of these samples showed a thick white layer constituted by calcium carbonate (calcite) covered by a red colored layer. The pigment used was hematite. The EDX analysis showed the presence of Cl in these cross-sections. A small layer constituted by calcium sulphate dehydrated (gypsum) appeared on the surface.

A thin layer of stucco may be applied with brush to reproduce the same original texture of the stone. The thin layer of stucco, due to its content in lime, protects and embellishes the stone with its color (the original or modified).

## 4. Conclusions

The petrographic study showed the presence of thin grained carbonate constituted essentially by bioclasts and fine sand. The SEM study showed a compact and continuous layer probably polymeric. The infrared spectroscopy study confirmed presence of an acrylic resin, which sometimes covers a black crust constituted by alkanes characterized by mass spectrometry. In addition microspherules were found. These compounds were attributed to environment contamination produced by combustion. Reposition material was observed covering or fixing some pieces of stone. The study by XRD and IRTF confirmed the presence of gypsum. Mortars constituted by calcite (60%) and inert material (40%; mainly quartz, feldspars and mica) were also characterized. In some parts of the façade some possible wall paintings were detected. They was constituted by a yellowish layer of Ca ($CaCO_3$) and covered by a thin grey layer performed by S and Ca (gypsum) due to contamination. In some parts, a red layer performed with iron oxides was also found in the wall paintings. Sodium chloride was also characterized.

## Acknowledgements

The authors are indebted to the Patronato de los Reales Alcazares de Sevilla for the collaboration with the present investigation. The financial support of the Spanish Commission interministerial de Ciencia y Tecnología (CICYT) under project BIA2009-12618 and the Junta de Andalucía (TEP-6558) are also acknowledged.

## References

[1] Guerrero Montes MA. Diagnostico del estado de alteración de la piedra del Palacio Consistorial de Sevilla. Causas y Mecanismos. Universidad de Sevilla 1990.

[2] Barrios Padura A, Barrios Sevilla J, Garcia Navarro J. Alteraciones en la fábrica de piedra de la sala capitular del Ayuntamiento de Sevilla. *Materiales de construcción***,** 2006; **284**: 87-94.

[3] Durán A., MD. Robador, M. C. Jiménez de Haro, L. K. Herrera, P. Gimena, J. L. Pérez-Rodríguez. Seville City Hall Chapter Room ceiling decoration. *Materiales de Construcción*, 2010; **60**: 83-95.

[4] Saiz-Jiménez C. Deposition of airbone organic pollutants on historic buildings. *Atmos. Environ*, 1993; **27**: 77-85.

[5] Perez-Rodriguez JL, Maqueda C, Jimenez de Haro MC, Rodriguez-Rubio P. Effect of pollution on polychromed ceramic statues. *Atmos. Environ* 1998; **32**: 993-998.