European Journal of Science and Theology, October 2015, Vol.11, No.5, 285-296

ANALYSIS, DIAGNOSIS, CONSOLIDATION AND WATER REPELLENT TREATMENT OF THE BURGOS CATHEDRAL STONE

María Dolores Robador[1] and Jose Luis Pérez-Rodríguez[2,*]

[1] *Technical Architecture Faculty University of Seville, Avda Reina Mercedes s/n, 41012 Seville, Spain*
[2] *Materials Science Institute of Seville (CSIC-Sevilla University), Americo Vespucio 49, 41092 Seville, Spain*

(Received 17 December 2014, revised 16 May 2015)

Abstract

A characterisation and alteration study of the Burgos Cathedral stone has been performed. In addition, the advantages and disadvantages of different consolidating and water repellent treatments applied to the stone were discussed. The chemical analysis suggests that the samples taken from the quarry and the monument consist of high-purity limestone (99.4% and 97.8% biosparite). The density, porosity, sorption-desorption behaviour, capillarity and permeability were determined. The obtained results showed the presence of free pores that facilitate the movement of water through stone. The mortars are mainly composed of SiO_2 and CaO, with a high content of lime (calcite) and sand (quartz). The following alterations were found in the stone surface: patinas, black crusts, blistering, disaggregation, disintegration, efflorescence, surface deposits, chipping, alveolar erosion, fissuring and vegetation. The cartography of alterations was described. Four zones of white or washed stone, grey or dry deposits, black or wet deposits and green-yellow deposits were observed. The stones from quarries and monuments are treated with different consolidating and water repellent treatments that include silico-organic preparations, acrylic resins and fine mortar ('jabelga'). The best results were obtained using 'jabelga'.

Keywords: stone, properties, alteration, consolidant, jabelga

1. Introduction

Burgos Cathedral (Figure 1) is a Gothic-style Roman Catholic Cathedral in Burgos, Spain. Its construction began in 1221, and the work continued intermittently until 1567. It was built in the French Gothic style, although Renaissance-style works were added duringn the 15^{th} and 16^{th} centuries [1]. The cathedral was declared a World Heritage Site by UNESCO in 1984. The building was constructed entirely of stone obtained from the Hontoria de la Cantera quarries. The white stone used in this Cathedral is one of its remarkable

*Corresponding author, e-mail: jlperez@icmse.csic.es

components. The composition of the quarry is primarily limestone from the Cretaceous period. It was necessary to assess the mechanical properties of the materials in order to establish constitutive laws for decayed materials, to develop methods for analysing damaged structure and to improve reliability criteria.

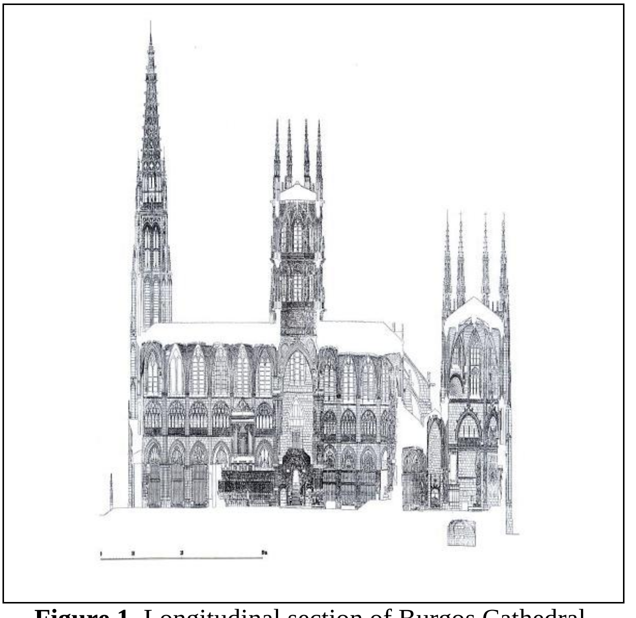

Figure 1. Longitudinal section of Burgos Cathedral.

Prevention and restoration can be successfully accomplished only after a careful diagnosis of a building damage. Accurate material characterisation improves knowledge of the building's material, increases understanding of its structural behaviour and facilities the development of successful interventions for consolidation and protection through water repellent treatments [2, 3].

The main weathering factors of the stone that can be differentiated are endogenous or exogenous. Man favours decay through pollution or direct treatment. In these cases, he can also act to protect and restore materials from decay.

Several studies have shown that the surfaces of buildings may be covered by environment pollutants and/or by substances produced during the alteration processes. The observation and description of the macroscopic decay indicators of stone are highly useful techniques to evaluate the extent and severity of damage [4]. Consolidation and water repellent treatments are frequently applied to the stonework at cultural heritage sites. One of the components of these restoration processes is stone protection by means of hydrophobic products, mainly organosilicic and acrylic products [5]. A thin layer of fine mortar composed of lime and some pigment, such as iron oxides, has also been used to protect the stone [2, 3]. The technique of applying coatings based on lime mortar is ancient and was applied as protection for façades of various materials, including stone. This protection was applied until the last century. The nonapplication of this technique is responsible for the deterioration of many monuments. Several factors must be considered in the application of consolidating products, such as the consolidating value, depth of penetration, effect on appearance, compatibility of consolidation with substrate, durability of treatment, effect on liquid water and vapour permeability, biological resistance, easiness of application, and health and safety issues [6].

This study aimed to do the following: 1) physically and chemically characterise the stone and mortars, 2) investigate the alterations that have developed in the stone, 3) apply consolidating and water repellent treatments to the stone, and 4) characterise the advantages and disadvantages of different products that were applied.

2. Materials and methods

2.1. Materials

Several stone samples were taken directly from the quarry and 13 samples from the different zones of the building (from the facade, the tower and the dome). 14 samples of mortars were also taken from the building.

2.2. Methods

2.2.1. Chemical analyses

The determination of the percentages of calcium oxide (CaO), silica (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3), magnesium oxide (MgO), sulphates (SO_3) and material lost on ignition (LOI) in the stones was conducted according to standardised test described in UNE-EN 196-2:2006 [UNE-EN 196-2:2014, *Métodos de ensayo de cementos. Parte 2: Análisis químico de cementos*]. The determination of chloride (Cl^-) percentage was conducted according to the standard test described in UNE 83-124-90 [UNE 83-124-90, *Áridos para hormigones. Determinación cuantitativa de cloruros. Método volumétrico*]. The determination of the percentages of ammonia (NH_4), nitrites (NO_2) and nitrates (NO_3) was performed with the Dr. Lange test cubes. The weight proportion of lime was calculated according to the following equation:

$$1.32 \text{ x } (\%CaO - 07\%SO_3) = \%Ca\,(OH)_2 \qquad (1)$$

The pH was measured using a pHmeter, HANNA NEURTEX MODEL HI 8314.

2.2.2. Physical tests

Bulk density and porosity were determined according to the standard test described in (UNE 83-820-94) [UNE-EN 1936:2007, *Morteros. Métodos de ensayo. Morteros endurecidos. Determinación de la densidad aparente*]. The adherence was determined according to the standard test described in UNE 83-

822 [UNE 83-822:1995, *Morteros. Métodos de ensayo: morteros endurecidos. Determinación de la adherencia de los morteros de revoco y enlucido*]. The granulometry of the aggregates was determined according to the standard test described in UNE 146110 specifications [UNE-EN 13139:2003, *Áridos para morteros. Definiciones y Especificaciones*]. Shear resistance tests were performed according to the standard described in (UNE-EN 103401) [UNE-EN 103401:1998, *Determinación de los parámetros de resistentes al esfuerzo cortante de una muestra de suelo en la caja de corte directo*]. The coefficient of absorption and desorption was obtained according to the standards described in (UNE 67027:1984, UNE-EN 771-1) [UNE-EN 67027:1984, *Ladrillos de arcilla cocida. Determinación de la absorción de agua*; UNE-EN 771-1:2011, *Especificaciones de piezas para fabrica de albañilería*]. Compresive and permeability tests were performed according to UNE-EN 1926 and E-ENE 15803, respectively [UNE-EN 1926: 2007, *Determinación de la resistencia a la compresión*; UNE-EN 15803: 2010, *Conservación del patrimonio cultural. Métodos de ensayo. Determinación de la permeabilidad al vapor de agua*].

2.2.3. Consolidant and water repellent treatments

Three different treatments were tested: i) an organosilicic consolidant followed by an organosilicic water repellent, ii) an acrylic polymer consolidant and iii) a consolidant and water repellent consisting of a fine lime mortar (‘jabelga’). The organosilicic and acrylic polymers were applied by immersion and spraying. The fine lime mortar was applied with a brush. Cubic samples of 5 cm were used for the entire test. These samples were obtained from blocks of stone from the quarries and the monument.

Before applying the products, the samples were cleaned, wetted and left in the air to dry until the water content was 0-2 g. The samples were treated by immersion for ten minutes to reach a uniform penetration on all faces.

3. Results and discussion

3.1. Quarry and monument stone

3.1.1. Chemical composition

The chemical analysis results suggested that the samples taken from the quarry and the monument are both high purity limestone (99.4% and 97.8% of $CaCO_3$). The percentages of sulphates and chlorides are somewhat higher in the samples from the monuments (0.66% and 0.08%, respectively) than those from the quarry (0.01% and 0.01%, respectively) due to environmental contamination. The percentages of SiO_2, Al_2O_3 and Fe_2O_3 (0.2%, 0.1% and 0.06%, respectively) were very similar for both stones.

3.1.2. Mechanical and physical properties

There were no differences between the density values of the monuments and the quarry stones (2.07 g/cm^3). The quarry stone was more porous than the monument stone (13.9% and 12.7%, respectively). Compressive test measurements in dry conditions and under water saturation returned higher values for the quarry stone (96.4 kg/cm^2 and 84.3 kg/cm^2, respectively) than the monument stone (80.1 kg/cm^2 and 67.3 kg/cm^2, respectively). The absorption rate in the quarry stone was very high, absorbing 3.2% in the first minute (43.2% of the total water absorbed), while the stone monument absorbed 2.35% (36.5% of the total). Increasing the amount of time of immersing in water to three hours increased the water absorption to similar values for both stones to 6.9 % (94.6% of the total) and 6.0% (95% of total) for the quarry and monument stone, respectively. The higher absorption rate in the quarry stone can be attributed to the greater number of free pores. Water desorption occurs in reverse order. The new quarry stone loses water more slowly than the monument stone. These results are explained by the larger fraction of pores in the quarry stone.

Capillarity - after three hours, the water reached 10-12 cm for the test specimen. Permeability - after two hours, the water had flowed through the test specimen. These results show the presence of pores that facilitate the movement of water through the stone.

The high absorption rate due to the great number of free porous and the values of capillarity and permeability recommended the applications of consolidants and water repellents.

3.2. Lime-based mortars

A study of the mortars of the Burgos Cathedral was performed. A large variation in the bulk density was observed (1.43-2.3 kg/l), mainly influenced by the particle size and the binder/aggregate ratio. In the mortars bearing the ashlars, the aggregate grain size was larger than the coating mortars, and they required less lime. For both of these reasons, their densities were typically higher. The density is also influenced by the mixing of the components and their technical implementation.

Porosity affects the hardness, water retention capacity and capillary water absorption. Furthermore, the higher porosity allows for a larger contact surface and more reaction with the gaseous pollutants, which influences the hardening and subsequent degradation of the material by atmospheric carbon dioxide. However, low porosity delays the carbonation process and hinders breathability. In lime mortars, equilibrium between both factors must be achieved. The older mortars had a pH value close to 7. High lime content generates more alkaline mortars (pH approximately 8). In isolated mortars, carbonation is difficult, so the pH of these samples remained approximately 8. Lime is high-purity calcium hydroxide, which gives great plasticity to the walls. The magnesium content in all samples was 0%, indicating that the lime was derived from the calcinations of high purity limestone and not from dolomite. The silica was also characterized by high purity and usually accompanied by feldspars, which are not harmful to the mortar. The silica grain size was appropriate to the application: thin for coating mortars, medium for ashlar-bearing mortars and thick and heavy for the bearing of the foundation. Gypsum, in particular, appeared in bearing mortars and the protective external mortar coatings. In bearing mortars, it is an intended addition to accelerate the hardening of the mortar and vertically expedite performance. In external coatings, some of the gypsum comes from the chemical reaction of the lime with aggressive environmental compounds, and the rest may be due to intentional addition, even if it means loss of durability in a city with abundant rainfall and low temperature. Aggressive chemicals such as ammonia and nitrites only occurred at trace levels. Chlorides and nitrates occurred in low proportions. This result may be due to the presence of these substances in the original kneading water or to further contamination. The binder aggregate ratio depends on the type of mortar developed and the function of each mortar.

Mortar samples were taken from exterior and interior of Burgos Cathedral. Theses samples were divided into four main groups.

3.2.1. Mortars bearing slab foundation

These mortars incorporated a small percentage of gypsum and they have low amounts of lime. We can guess that these mortars have not been compacted and possibly beings slabs of great, size and a thickness of 10 cm, they carry a settlement by weight rather than by adherence, and commissioning work was entrusted to the gravity setting. This way of conceiving the stone pavements settlement takes poor mortar used, because it is thought that heavy-weight stone system need not grip, but fixation is entrusted to be the weigh of the slab. The inequality of the thickness of the paving slabs made it necessary to look horizontally with equal quantity of mortar, varying percussion work to lay each piece.

3.2.2. Mortar of inner part of walls and bearing of ashlars

This mortar was used for the agglomeration of stones of the inner part of the walls of the cathedral to join ashlars. Dosing is higher in lime (slightly hydraulic, as evidenced by their content of aluminium oxide and iron oxide). This mortar has not been developed and implemented with the same care of bearing and coating mortars because their function was only filling agglomerated stones and giving the wall greater plasticity. Lime mortar provides a link between the seat stuffed inside the establishment, ensuring consistence between the veneer and solid breaks and avoiding different behaviour by ensuring the stability of the building.

3.2.3. Joining of aslars

The thickness of the mortar joints of the walls ranges from 0.9 to 2.5 cm (mostly between 1 and 1.5 cm). The stone ashlars were not perfect or parallel each other and the irregularities were solved with thick mortar. The technical expertise of the builders of the Cathedral involves the use of fort lime mortar, confirmed by practice, that's why they were looking for the right raw materials and employing the most suitable techniques for each application. These mortars are rich in lime to confer plasticity and to absorb the deformations of these great walls. The behaviour of lime mortars used in the union of the elements of these large buildings is comparable to the role on a bony skeleton of the elastic cartilage connecting the various elements of the skeleton, join parts without losing elasticity.

3.2.4. Coatings mortars

In the cathedral there are coatings mortars: exterior and interior coating. Although the stone itself has a compact good quality being carved with great wealth, it shows a great vulnerability to the attack of external aggressive agent. To avoid the deterioration that could occur the building constructors used lime mortar coatings for protection. They knew they had to protect the stone carved with something that defend against the destructive action of the environment through a mortar coating. These mortars called 'sacrifice' for their protective function, were periodically removed. The practice was lost with consequent unfortunate results.

3.3. Study of alterations to the surface of the monument

The study of the Cathedral of Burgos included an inventory of each form of alteration, which has been conveniently presented in maps to facilitate the work of restorers.

3.3.1. Inventory of the alteration forms

Various classes of patinas were observed in the Cathedral of Burgos. Table 1 shows Inventory of each form of alteration observed in Cathedral of Burgos. Chromatic patina: the stone of the Cathedral presents an ochrecolour due to the surface finishing given by 'jabelga'. A grey colour appears because of the adhesion of contaminants in areas not affected by rain. There is also, in some areas, a black colour that may be attributed to the start of the chemical deterioration of the substrate. In localised areas, a green patina appears that is induced by metallic copper compounds. Biogenic patina: very thin films are formed by living organisms that develop on the surface of the stone, such as lichens and mosses. The colour depends on the time of year and the cycle, ranging from dark brown to yellow. Discolouration patinas: Colour loss is observed due to rain and other pollutants that remove part of the protective layer and jabelga used for stone protection.

Chromatic patinas	Black crust	Other stone alteration
'jabelga', grey colour, black colour, green patina, biogenic patina, discolouration	lichens, dust adhesion (bound by gypsum, that develop algae, lichens, etc.)	blistering, surface deposit (organic or inorganic), caving, efflorescence, disaggregation, chipping, alveolar erosion, fissuring, vegetation

Table 1. Inventory of each form of alteration observed in Cathedral of Burgos.

On the façade of Burgos Cathedral, exposed to NNE, black crusts generated by lichens were present, beside other crusts formed due to dusts adhesion to the surface of the stones. This powder, usually clay found in a suspension form in the atmosphere, is bound by gypsum and forms a substrate that develops algae, lichens, etc., which grow on the surface and feed on the stone that supports them.

Other stone alterations observed. Blistering: this alteration is produced by deformation of the surface of the stone and is characterised by the formation of numerous bumps. Disaggregation: these material losses are the result of the loss of coherence between substance's components of different particle sizes. The degree of this form of deterioration of the stone material is very high due to the stone's porosity. Caving: this phenomenon is the result of a breakdown of the superficial stone due to the total loss of cohesion between its components. Efflorescence: deposits or layers of soluble salts appear on the surface cause important damage to stone and contribute to the formation of skin blisters. These are quite abundant in the Burgos Cathedral. This efflorescence is produced by a chemical attack on the stone, resulting in a loss of mass. Surface deposits: materials of diverse origin (organic or inorganic) accumulate on the surface of the stone; bird's excreta are included in this group. Chipping: the lift and separation of scales in parallel to the surface of the stone are produced by changes in humidity, temperature, ice movement, soluble salts, etc. Alveolar erosion: globular cavities form on the stony surface. Disaggregated stone material is usually located inside the cavities. These alterations are found in the lower areas of the Cathedral, on the façade of the Coronería. Fissuring: planar discontinuities, fractures or cracks of varying size and of different origins commonly develop in the mortar joints. Abundant fissuring appears in the Cathedral of Burgos due to oxidation and swelling of the sculptures' metallic holding. Vegetation: grasses, mosses, and even shrubs develop on the stones of the buildings and produce stone alterations. The roots produce fissures that fragment the stony substrate.

3.3.2. Alterations cartography

The cartography was carried out by visual observation. White zone or washed stone: the forms of alteration that dominate this area are discoloration of the stone due to washing without an observed loss of thickness. The development of these alteration forms depends on the situation and orientation of the stone (reliefs, faces runoff, etc.). Most stones retain their consistency, and the alteration degree can be considered low. However, a few zones do appear to have notable mass loss, especially under reliefs and sculptures. Grey areas or dry deposits: these zones can be found in the areas of the building protected from rain and runoff. The surface of the stone is subjected to continuous deposition from the environment. The stone is not altered because the surface deposits do not react chemically with the surface of the stone. Black areas of wet deposits: these areas appear in protected zones that are next to rain areas. These zones are characterised by constant humidity. Exogenous deposits are retained in these areas because of their reaction with the stone. These areas exhibited notable alterations, mainly crusts that evolved and gave rise to desegregations associated with efflorescence. The zones most favourable to these processes are the interiors of the cornice and outgoing. Green-yellow zones: these zones appear in areas of the building exposed to rain and heat. Plants, lichens and algae have developed there. Figure 2 shows a photo carried out before the façade restoration. It is shown clearly the orientation effect on the alteration. The south-west façade show white colour due to erosion of rain water and environmental contamination that produce the alteration of this façade zone. On the other hand the south west façade show a black superficial crust. In this zone of the building appear absorption water by capillarity and do not receives sunlight directly. In addition receive environmental contamination due to cars traffic.

Figure 2. White and black alteration.

3.4. Consolidants and water repellents applied to the stone

Water absorption was reduced considerably by the spraying treatment with organosilicic consolidant + organosilicic water repellent and by the treatment through immersion in the acrylic consolidant. The absorption was very high in the treatment through immersion or spraying with only the organosilicic consolidant. The results of acrylic consolidant application were not promising when performed by spraying and showed better results by immersion or saturation. The 'jabelga' application significantly reduced water absorption. The capillarity of stones from the quarry and the monument were reduced to zero in the case of the organosilicic consolidatant + organosilicic water repellent applied by spraying. Similar results were obtained with the acrylic consolidant treatment. The stone treated with 'jabelga' exhibited a capillarity reduction to half or one-third. The quarry and the monument stones treated with the organosilicic consolidant + organosilicic water repellent by spraying significantly exhibited improved durability against thermal treatments. However, the high cost of these products and their short durability limits their application. The acrylic consolidant shows deficient results when it is applied by spraying. The immersion of the stone monument is not viable, and the high cost of this product prohibits the use of this treatment.

The surface of the carved stone is greatly vulnerable to the attack of external aggressive agents. To avoid the possible occurrence of deterioration, the building construction utilised a lime mortar coating for protection as was previously described in lime-based mortars chapter

The builders knew that they had to protect the carved stone with something that could defend against the destructive action of the environment and used a mortar coating. These mortars were called 'sacrificial' for their protective function and were periodically reapplied. That practice was eventually lost, with regrettable results.

The 'jabelga' used in our work as a consolidant and water repellent has proven its effectiveness compared to the organosilicic, and the organosilicic and acrylic polymer treatments. This treatment gives the stone a good protection. This treatment (jabelga) has two main advantages: its durability and a good behaviour over time, which have been demonstrated by previous treatments carried out on the monument for centuries [7]. The low cost and easy application of this material showed the advantageous in comparison with the other products used in this work. Pigments can be added when they are required. The control of application is very easy. It is possible to distinguish those areas that are protected from those that are not.

4. Conclusions

The stones analyzed in this study came from the quarries and the monument and are made of high-purity limestone. The high retention of water in the open pores can cause freezing alteration and dissolution phenomena. The capillary rise of water and easy circulation is important in this stone. The mortars are mainly composed of SiO_2 and CaO, with a high content of lime and sand. Quartz and calcite are present in almost all samples. According to the present study, there were probably very strict rules and an extensive knowledge of the components of mortars and their performance.

Cathedral builders chose materials with great skill. The lightness, transparency, and stability achieved by the Burgos Cathedral were achieved by bonding the stones with lime mortar.

Patinas, black crust, pitting, disaggregation, detachments, efflorescence, surface deposits, grain desegregation, cracking and vegetation have been observed in the monument and are responsible for the stone's alterations. The cartography of the alterations helped to elucidate four main categories: white or washed stone, grey or dry deposits, black or wet deposits and green-yellow areas.

Different consolidants and water repellents were tested in this study: i) an organosilicic consolidant followed by an organosilicic water repellent, ii) an acrylic polymer consolidant and iii) a consolidant and water repellent consisting of a fine lime mortar (jabelga). The 'jabelga' applied by brush showed significant advantages relative to the other products used.

Acknowledgment

The financial support of the Spanish Comision Interministerial de Ciencia y Tecnología under project BIA2009-12618 and the Junta de Andalucía (TEP-6558) are acknowledged. The authors wish to thank Mr. R. Pérez-Maqueda for the typing and composition of the manuscript.

References

[1] M.D. Robador. *El revestimiento de la piedra de la Catedral de Burgos*, Proc. Of the II Congreso Nacional de Historia de la Construcción, F. Bores, J. Fernandez, S. Huerta & E. Rabasa (eds.), Instituto Juan de Herrera. Universidad de A Coruña, Coruña, 1998, 417-429.

[2] M.D. Robador, F. Arroyo and J.L. Perez-Rodríguez, Constr. Build. Mater., **53** (2014) 370-380.

[3] P. Pineda, M.D. Robador and J.L. Pérez-Rodríguez, Constr. Build. Mater., **43** (2013) 612-633.

[4] R. Esbert and R. Marcos, Mater. Construcc., **186** (1982) 79.

[5] M. Alcalde Moreno, R. Villegas Sanchez and J.E. Vale Paropar, *Study on weathering and conservation treatments for the Stone of Andalusian Monuments. Macroscopical Morphology of Accelerated Weathering of Some Petreousmaterials*, in *Applied Study of Cultural Heritage and Clay*, J.L. Perez-Rodriguez (ed.), CSIC, Madrid, 2003, 259-288.

[6] E. Hansen, E. Doehne, J. Fidler, J. Larson, B. Martin, M. Matteini, C. Rodríguez-Navarro, E. Sebastián Pardo, C. Price, A. de Tagle, J.M. Teutonico and N. Weiss, Reviews in Conservation, **4** (2003) 13-25.

[7] M.D. Robador, *Los Revestimientos en la Antigüedad*, in *La Técnica de la Arquitectura en la Antigüedad*, Universidad de Sevilla, Sevilla, 1998, 193-209.