

THE CATHEDRAL OF SANTA MARÍA (CUENCA, SPAIN): PRINCIPAL STONE CHARACTERIZATION AND CONSERVATION STATUS

Enrique TORRERO¹, David SANZ*¹, M^a Nieves ARROYO¹, Vicente NAVARRO²

¹Polytechnic School of Cuenca, University of Castilla-La Mancha, Campus Universitario, s/n. 16071. Cuenca. Spain

²Civil Engineering School, University of Castilla-La Mancha, Edificio Politécnico, 13071. Ciudad Real. Spain.

Abstract

The Cathedral of Santa María of Cuenca is one of the earliest Gothic cathedrals in Spain. The stone used in its construction mostly came from a quarry (now abandoned) in Arcos de la Cantera. It is a white lacustrine limestone with two lithotypes coded as hard (H) and soft (S). The two have similar chemical compositions, but type H has minor quartz, which type S lacks. There is also a small difference in the chromaticity in type S with respect to type H. The pore size ranges from 0.1 to 1 μm for type H and from 0.1 to 20 μm for type S. The conservation status of this stone depends on the lithotype and on the location of the stone in the monument. Type S is the most heavily affected by honeycombing. Inside the Cathedral, there is also abundant salt efflorescence due to both absorption and porosity.

Keywords: Cathedral; Cuenca; Limestone; Pore Structure; Durability; Conservation Status

Introduction

The city of Cuenca lies in the centre of the Iberian Peninsula midway between the Mediterranean coast and the central plateau. The historic centre of Cuenca is currently a first-class architectural ensemble listed as a World Heritage Site by UNESCO in 1996. The most representative monument of the old town is the Cathedral of Santa María of Cuenca (Fig. 1). Work on the Cathedral of Cuenca started in the late twelfth century (1183–1195) and was finished in the second half of the thirteenth century (1257). One of the most important aspects of this cathedral is the coexistence of three distinct styles — the *Romanesque*, the new *Gothic* techniques coming from France, and later the *Baroque* [1].

Stone selection in historical buildings and monuments is not a random choice for builders and architects [2]. Stone materials used in the construction in the Cathedral of Santa María of Cuenca were selected by its characteristics of colour and texture, and also by its physical properties. This appearance is lost over time, so it is necessary to act in order to restore its original appearance and stop the degradation process (Fig. 2).

The climate in the city of Cuenca is continental-Mediterranean, cold in winter (mean: 6.3°C and min: -17.8°C) and mild in summer (T mean: 18.8°C and T max: 39.7°C). Mean rainfall is over 500 mm/yr, falling mainly in autumn and spring, and mean relative humidity is 60%. The mean wind speed is 11 km/h and affects all the walls of the cathedral regardless of their orientation [3]. Biological activity in the cathedral is of animal and vegetable origin.

* Corresponding author: David.Sanz@uclm.es

Animal activity mainly involves surface deposits of pigeons in wall projections. Plant activity comprises higher plants, algae and lichen colonies growing on the roofs, walls, and rainwater gutters. Apart from the weather, environmental pollution is another important factor in the natural stone decay. These are the main factors involved to different extents in relation to the decay of stone materials [4].

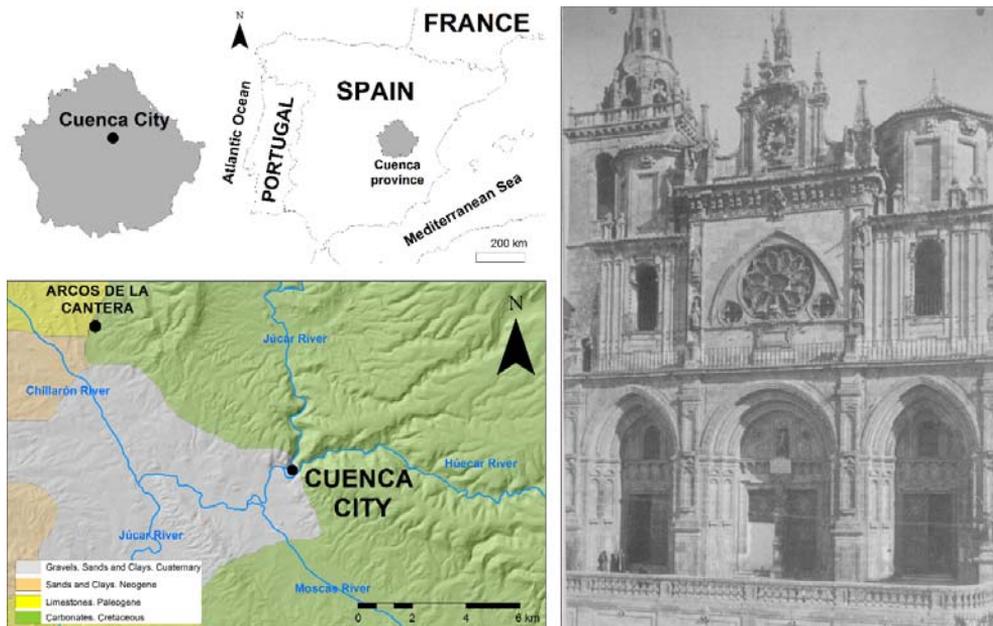


Fig. 1. Location of The Cathedral of Santa María of Cuenca (left) and the main facade baroque made with Stone of Arcos de la Canteras before its collapse in 1902 (right). Photo taken by Aregre.



Fig. 2. Common pathologies in the Stone of Arcos de la Canteras located at the Cathedral of Cuenca: a - Alveolar erosion, b - Salt efflorescence

However, decay of natural stone in monuments and historic buildings is not only produced by the environmental conditions, but is also influenced by the petrophysical characteristics of the material and, mainly by its hydric behavior that come through the porous structure [5]. This paper has made a detailed study of one of the most used stone materials in the Cathedral of Santa María of Cuenca. On the one hand, the stone material located in the

architectural complex has been recognized and characterized with its place of origin (historic quarries). Furthermore, the petrophysical characteristics of the material have been analyzed in order to predict its physical behavior, durability and thus its state of preservation.

Materials and methods

The location of the original quarries of stone materials used in the architectural heritage is an essential aspect in the petrological study of a building as has been demonstrated in numerous studies such as those of [6-10]. In fact, it is common to compare the state of deterioration of the building stone with respect to the samples of historical quarries and in some cases they may be studies on aging or behaviour to various consolidation treatments. The city of Cuenca is located on Upper Cretaceous dolomitic limestone. However, most of the stone used in the construction of the cathedral comes from the town of Arcos de la Cantera about 8 km away (Fig. 1), which for centuries has served as a stone supplier for the cathedral [11]. Today, the quarry is abandoned and difficult to access. Table 1 classes the stone used in the different parts of the cathedral by lithology and place of origin. We have studied the stone from Arcos de la Cantera as it is by far the most common stone used in the cathedral (> 80%).

Lithologically, the stone is lacustrine white limestone stratified in decimetric layers alternating with grey marl beds of up to 5 metres thick. These deposits can be up to 80 metres thick in the quarry. Based on fossil contents and stratigraphic position, the age is Neogene (11 Ma). Within these materials, two lithotypes can be distinguished based on appearance, termed hard (*H*) and soft (*S*). Sufficient materials for laboratory tests were collected from the historic quarry of Arcos de la Cantera and from the cathedral.

Table 1. Inventory of stone used in the Cathedral of Santa María of Cuenca. Sources: [15, 16, 17 and 11].
* Reconstruction early SXX, formerly origin of *Arcos de la Cantera*.

Name and Source	Lithology	Location in the Cathedral
Carrara, Italy.	White marble.	Altorrelieves. Altar of the Mayor Chapel.
Buenache, Cuenca-Spain.	Red Dolostone.	Sagrario Chapel.
Granada, Spain.	Serpentine.	Altar Mayor of the Cathedral.
La Cierva, Cuenca-Spain.	Dolostone and jasper.	Altar Mayor and Sant Julian Chapel.
Torrubia, Cuenca-Spain.	Dolostone and limestone.	Access steps of the Cathedral *
Novelda, Alicante-Spain.	Biocalcarenite.	West facade of the Cathedral *
Júcar Huécar, Cuenca-Spain.	Dolostone and limestone and tobas.	Back of the Cathedral and episcopal palace
Húecar, Cuenca-Spain.	Grey marly limestone.	Cloister
Júcar Huécar, Cuenca-Spain.	Dolostone and limestone.	Back of the Cathedral and floor
Arcos de la Cantera Cuenca-Spain.	Lacustrine limestone.	80 % Cathedral. Ashlar and ornaments.

The chromatic characterization of the samples was performed using a spectrophotometer Chroma Meter CR-410, obtaining tristimulus values, chromaticity coordinates (X, Y, Z), luminance (L*), chromaticity (a* b*), colour (C*), and hue angle (H*). The chemical, mineralogical, and textural studies (stones and salt efflorescence) were performed using, respectively: (a) X-ray fluorescence spectrometry (Philips Magix Pro model), (b) X-ray diffraction (XRD, Philips X'Pert MPD diffractometer model), and (c) polarized light microscopy.

Water performance tests were conducted to determine the coefficient of water absorption by capillarity (1999 UNE-EN 1925), water absorption at atmospheric pressure (UNE -EN 13755: 2008), real and apparent density, and open and total porosity (UNE - EN 1936: 2007). Porosity was established by mercury porosimetry injection using a Micromeritics Autopore IV model 9500. Finally, for the durability studies, samples were tested for resistance to freezing (EN 192371: 2011) and salt crystallization (EN 12370: 1999).

Results and Discussions

Petrological properties

Both lithotypes are a limestone formed by the precipitation of calcium carbonate in lacustrine environments and range in colour from white to beige (see Table 2). There is uniformity in the samples for L^* and H^* and a noticeable difference in a^* , b^* , and C^* of lithotype S (more beige) with respect to type H (whiter) (Fig. 3a).

Table 2. Tristimulus values (X, Y, Z), Chromaticity coordinates (x, y), Lightness (L^*), Chromaticity (a^*, b^*), color (C^*) and hue angle. Limestone quarry ($S; H$) and the Cathedral ($S; H$).

Source	Code	X	Y	Z	x	y	L^*	a^*	b^*	C^*	H^*
Quarry	S	49.22	49.75	44.41	0.34	0.35	76.02	1.18	14.22	14.27	85.14°
	H	53.04	53.14	54.93	0.33	0.33	77.95	1.92	7.10	7.36	74.61°
Cathedral	S	52.68	53.20	45.69	0.35	0.35	77.77	2.10	16.22	16.36	82.68°
	H	47.66	48.43	47.38	0.33	0.34	75.05	0.46	9.62	9.65	87.27°

As pointed [12], optical Microscopy and XRD provide rapid characterization of the main constituents of samples heritage that can be used to determine the origin of these. In this sense, results indicate that calcite is the major mineral in both types of samples (H and S) from the quarry and the cathedral. In H samples, a peak in the diffractogram corresponding to quartz is also evident (Fig. 3b). The texture of the samples from the cathedral and the quarry (Fig. 3c) is that of a micritic limestone. The chemical composition of the two lithotypes is similar, comprising in both cases a fairly pure limestone high in calcite (Table 3). In the H samples, oolites (about 10 μm in diameter) are enveloped by calcite with a low crystalline index. Often, those cores are formed of quartz clasts. However, the chemical and mineral composition (SiO_2 present values that may correspond to quartz) found in H samples, has an influence in aspects like macroscopic morphology and therefore in hardness, durability and mechanical properties.

Respects, chemical analysis of salt efflorescence pathologies show a high percentage of sulphur and magnesium oxides. Probably these compounds come from the water filtered by the cover with contents of SO_2 and SO_3 (environmental pollution). When these compounds are in contact with limestone favour the dissolution and precipitation of calcium and magnesium sulphates salts (Table 3).

Table 3. Chemical composition of Stone samples and salt efflorescence (%). Limestone quarry ($S; H$) and the Cathedral ($S; H$).

Source	Code	CO_2	MgO	Al_2O_3	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	SrO	SiO_2
Quarry	S	43.63	0.15	0.32	0.01	0.23	0.03	55.28	0.27	0.05	-
	H	42.08	0.47	0.89	0.00	0.28	0.15	53.17	0.25	0.05	2.56
Cathedral	S	44.52	0.15	0.31	0.01	0.26	0.00	54.88	0.10	0.05	-
	H	44.26	0.09	0.13	0.00	-	0.01	54.95	0.13	0.03	0.36
Efflorescence	Ef	72.67	10.06	0.28	0.01	13.80	1.02	2.09	0.01	0.01	-

The porous structure or network of stone can be described as a bundle of pore throats (entrance) and chambers where the pore chamber is placed between the pore throats [13]. The porosity of each of the samples has been isolated by microscopy digital image processing. In both cases, a non-selective vug porosity factor was observed with chamber-and-throat pore sequences. Pore size is 1 to 10 μm in H samples and 0.1 to 20 μm in S samples. Porosity values are very similar to those found by other methods (Fig. 3d).

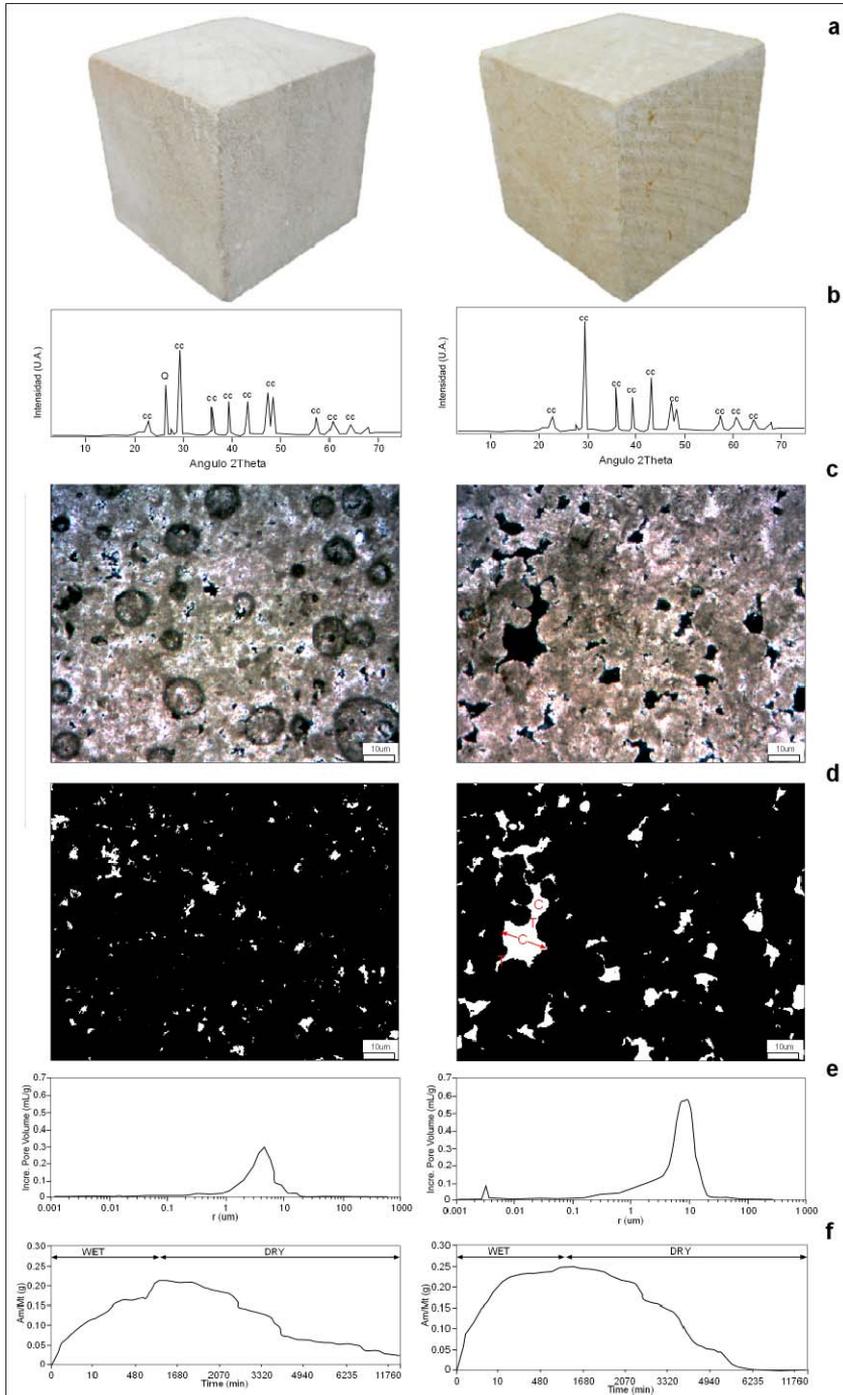


Figure 3. (Left): Lythotype Hard (*H*). (Right): Lythotype Soft (*S*). First (a): Photography appearance and color of the cubic samples (5 cm side); Second (b): Spectrum of X Ray diffraction, minerals Calcite (CC) and Quartz (Q). Third (c): Optical Microscopic images with crossed nicol; Fourth (d): Digital image processing to obtain porosity in color white with Throats (T) and chamber (C) pore sequence; Fifth (e): Pore size distribution. Increment of pore volume (Incr. Pore Vol) en mL/g. Logarithm of the pore radius μm . Sixth (f): Absorption-desorption of water at atmospheric pressure of the samples tested.

Petrophysical properties

There are differences in the hydric properties of the two different lithotypes of limestone (Table 4), which is also reflected in the absorption/desorption processes (Fig. 3f). The water absorption capacity of this type of rock is fairly high and, though higher in the *S* type, water also evaporates faster than in the *H* type. These aspects are directly related to the pore size and morphology. Most of the pores are in the range of micropores of 0.1 to 1 μm for type *H* and 0.1 to 20 μm for type *S*. (Fig. 3 d-e). These results confirm observations under light microscopy. Regarding their mechanical properties, lithotype *H* has an average compressive strength of 42 N/mm², whereas lithotype *S* has no more than 5 N/mm².

Table 4. Hydric trial findings. Bulk density (*Bd*) Real density (*Rd*), Porosity accessible to water (*P*), Free water absorption (*Abs*), Saturation (*S*), Capillary suction or Sorptivity (*Sorp.*), Effective porosity (*Effec. P*), Total porosity (*Total P*). Limestone quarry (*S*; *H*) and the Cathedral (*S*; *H*).

Source	Code	<i>Bd</i> (g/cm ³)	<i>Rd</i> (g/cm ³)	<i>P</i> (ml.)	<i>Abs</i> (%)	<i>S</i> (%)	<i>Sorp.</i> (g/cm ² s ^{-0.5})	<i>Effec. P</i> (%)	<i>Total P</i> (%)
Quarry	<i>S</i>	1,45	2,71	46,28	23,31	71,31	0,00406	33,06	46,49
	<i>H</i>	2,15	2,70	20,34	5,77	58,05	0,00114	11,3	20,37
Cathedral	<i>S</i>	1,49	2,74	51,45	19,97	92,21	0,005516	42,25	45,82
	<i>H</i>	1,89	2,63	27,78	13,53	57,98	0,004416	16,25	28,02

Durability

Freeze-thaw and salt simulation cycles have been used to estimate durability (Fig. 4). These processes are the main mechanism of degradation of a material exposed to external conditions [14]. The porous system and its distribution determine the availability of fluids inside, and so affects its durability. The results of freeze-thaw cycles (Table 5) show that the type *S* stone has a greater loss than type *H* by weight. The results from salt crystallization tests (Table 6) indicate that, within groups of Arcos de la Cantera limestone, type *S* has a poorer performance with greater weight loss and fewer cycles. However, type *S* has a better performance against salt crystallization, although that is also affected.

Table 5. Weights in grams (g) of samples subjected to freeze-thaw cycles. Dry Weight (*Wd*). Saturated Weight (*Ws*). Hydrostatic Weight (*Wh*). Increase in volume (ΔV). Broken samples (*). Lythotype Hard (*H*). Lythotype Soft (*S*)

<i>Code</i>	Initial Data			Post freeze-thaw cycles			
	<i>Wd</i> (g)	<i>Ws</i> (g)	<i>Wh</i> (g)	<i>Wd</i> (g)	<i>Ws</i> (g)	<i>Wh</i> (g)	ΔV (%)
S(1.6)	191,90	234,48	110,04	*	*	*	*
S(1.7)	189,29	231,32	106,92	187,21	238,25	114,01	0,129
H(2.1)	211,85	247,85	122,65	211,67	255,35	129,95	-0,16
H(2.2)	265,40	281,19	155,42	265,34	286,63	160,60	-0,207
H(1.6)	297,52	307,71	179,79	297,45	312,11	181,14	-2,384
H(1.7)	296,18	306,69	179,21	296,13	309,38	181,84	-0,047
S(2.6)	185,29	230,11	101,22	*	*	*	*
S(2.7)	191,47	233,38	107,62	*	*	*	*

Table 6. Weights in grams (g) of samples subjected to salt crystallization cycles (Na₂SO₄·2H₂O). Initial Weight (*Wi*). Final Weight (*Wf*). Increase in volume (ΔV). Broken samples (*). Lythotype Hard (*H*). Lythotype Soft (*S*)

<i>Code</i>	<i>Wi</i> (g)	<i>Wf</i> (g)	ΔV (%)
S(1.3.)	91,80	*	-0,34
S(1.5)	92,56	*	*
S(1.6)	92,75	*	*
H(2.1)	129,59	126,94	-2,04
H(2.2)	153,54	150,97	-1,67
H(2.3.)	115,80	112,60	-2,76
S(2.1.)	90,19	56,02	-37,89
S(2.5)	89,46	60,79	-32,05
H(1.4)	301,22	301,20	-0,01
H(1.5)	283,76	279,88	-1,36

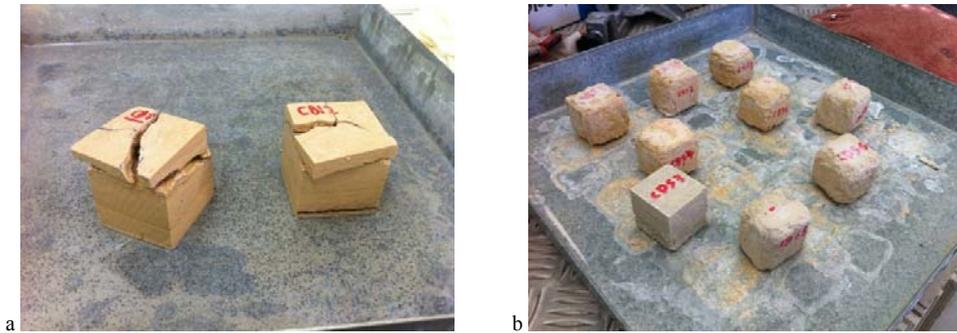


Fig. 4. Samples subjected to durability tests:
a) freeze-thaw cycles, b) salt crystallization cycles ($\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$).

Conclusions

The Cathedral of Santa María of Cuenca was built mostly with stone from Arcos de la Cantera, as confirmed by the chemical and petrological results. Two lithotypes, both in the quarry samples as in samples obtained from the Cathedral, have been located and have been classified as hard lithotype (*H*) and lithotype soft (*S*). The chemical composition is very similar in both lithotypes. It is a limestone with very low percentages of impurities but with the presence of SiO_2 in the lithotype (*H*). The study by microscopy and XRD indicated that calcite is the major mineral with quartz presence in the lithotype (*H*). Lithotype *S* usually has better workability and was used as a material for ornament frames, figures, and reliefs. Type *H* was used as the resistant material for load-bearing blocks and ashlar, and it is more resistant to degradation than *S* due to its lower porosity and smaller pore sizes. However, due to the porous structure of the system, both samples are susceptible to degradation by capillary inhibition, salt crystallization, and freeze-thaw cycles. In *S* samples with higher porosity, it is easier to absorb and evaporate the water, whereas in *H* samples the process is slower. The residence time of water in the samples, under the same conditions, is higher in *H* than in *S* samples.

The conservation status of the material from Arcos de la Cantera depends on the lithotype and the location of the stone in the cathedral (outside or inside). Outside, regardless of lithotype, there are black biological patinas, biological fouling, and vandalism. One of the most characteristic lesions in the *S* type is honeycombing (small pits less than 100 μm in diameter) caused by dissolution, or hydrolysis followed by dissolution of the main mineral calcite. Also appearing in the masonry walls and/or ashlar stonework is honeycombing with uneven pits no greater than 5 mm in radius (Fig. 2a). The most common pathology inside the cathedral is abundant salt efflorescence produced by various types of humidity that carry the salts and deposit them on the inside walls (probably the source of salts is environmental pollution). Type *S* is most affected because of its absorption capacity and porosity (Fig. 2b). Efflorescence thickness can reach up to 1 cm, but is easily removed.

Acknowledgments

This study is part of the PhD Thesis of D. Enrique Torrero. The authors wish to thank D. Miguel Angel Albares, Director of the Cathedral of Santa María of Cuenca for all the facilities and access to the monument, and D. Elias Alonso for his comments and help in field work.

References

- [1] F. Noguera Campillo, *La armadura de cubierta y el sistema de evacuación de aguas del brazo mayor de la catedral de Cuenca. Análisis constructivo y restitución teórica. Ph.D. Thesis* [In Spanish], University of Castilla – La Mancha, Spain, 2011.
- [2] L. Ventolà, P. Giraldez, M. Vendrell, *Selective use of stones in the medieval Cathedral of Tarragona, Spain: construction and historical reasons*, **International Journal of Architectural Heritage**, **6**(5), 2012, pp. 478-488.
- [3] * * *, **Agencia Estatal de Meteorología**, <http://www.aemet.es>, [accessed online 15.06.2015].
- [4] M. El-Gohary, *Physical deterioration of Egyptian limestone affected by saline water*, **International Journal of Conservation Science**, **4**(4), 2013, pp. 447-458.
- [5] D. Benavente, M.G. del Cura, R. Fort, S. Ordóñez, *Durability estimation of porous building stones from pore structure and strength*, **Engineering Geology**, **74**(1-2), 2004, pp. 113-127.
- [6] A. Banchelli, M. Fabio Fratini, P.G. Malesani, C. Manganelli Del Fa, *The sandstones of Florentine historic buildings: individuation of the marker and determination of the supply quarries of the rocks used in some Florentine monuments*, **Science and Technology for Cultural Heritage**, **6**(1), 1997, pp 13-22.
- [7] R. Dreesen, M. Duser, *Historical building stones in the province of Limburg (NE Belgium): role of petrography in provenance and durability assessment*, **Materials Characterization**, **53**(2-4), 2004, pp 273-287.
- [8] R. Fort, M. Álvarez de Buergo, E.M. Pérez-Monserrat, *Non-destructive testing for the assessment of granite decay in heritage structures compared to quarry stone*, **International Journal of Rock Mechanics and Mining Sciences**, **61**, 2013, pp 296-305.
- [9] C. Uhler, K. Schaller, M. Unterwurzacher, *Historic Quarries: Case Studies*, **Scientific Computing and Cultural Heritage, Springer Berlin Heidelberg**, 2013, pp. 245-253.
- [10] R. Navarro, J. Sánchez-Valverde, J.M. Baltuille, *The Natural Stone in the Historic Buildings of the City of Granada (Southern Spain). Features as a Possible Candidate for the Designation of “Global Heritage Stone Province*, **Engineering Geology for Society and Territory- Springer International Publishing**, **5**, 2015, pp. 229-232.
- [11] E. Torrero, D. Sanz, V. Navarro, *Porosity and Pore Size Distribution of the Dimension Stone in the Historic City of Cuenca*, **Construction and Building Research-Springer Netherlands**, 2014 pp. 523-529.
- [12] D.A. Silva, H.R. Wenk, P. J. M. Monteiro, *Comparative investigation of mortars from Roman Colosseum and cistern*, **Thermochimica Acta**, **438**(1-2), 2005, pp 35-40.
- [13] M. Angeli, D. Benavente, J.P. Bigas, B. Menéndez, R. Hébert, C. David, *Modification of the porous network by salt crystallization in experimentally weathered sedimentary stones*, **Materials and Structures**, **41**(6), 2008, pp. 1091-1108.
- [14] R. Příkryl, T. Lokajíček, J. Svobodová, Z. Weishauptová, *Experimental weathering of marlstone from Přední Kopanina (Czech Republic)—historical building stone of Prague*, **Building and Environment**, **38**(9), 2003, pp. 1163-1171.
- [15] J. Díez Bermejo, *La catedral de Cuenca*, [In Spanish] **Caja de Ahorros Provincial**, 1977.
- [16] M.L. Rokiski Lázaro, *Arquitecturas de Cuenca*, [In Spanish], **Servicio de Publicaciones de la Junta de Comunidades de Castilla-La Mancha**, 1995.
- [17] G. Palomo Fernández, Gema, *La Catedral de Cuenca en el contexto de las grandes canterías catedralicias castellanas en la Baja Edad Media*, **Ph.D. Thesis** [In Spanish] Universidad Autónoma de Madrid. Facultad de Filosofía y Letras; Universidad Autónoma de Madrid. Departamento de Historia del Arte, 1995.

Received: March, 12, 2015

Accepted: November, 10, 2015